इंटरनेट मानक

Disclosure to Promote the Right To Information

Whereas the Parliament of India has set out to provide a practical regime of right to information for citizens to secure access to information under the control of public authorities, in order to promote transparency and accountability in the working of every public authority, and whereas the attached publication of the Bureau of Indian Standards is of particular interest to the public, particularly disadvantaged communities and those engaged in the pursuit of education and knowledge, the attached public safety standard is made available to promote the timely dissemination of this information in an accurate manner to the public.

"जानने का अधिकार, जीने का अधिकार"
Mazdoor Kisan Shakti Sangathan
"The Right to Information, The Right to Live"

"पुराने को छोड नये के तरफ"
Jawaharlal Nehru
"Step Out From the Old to the New"

IS 15128 (2002): Natural Gas - Performance Evaluation for On-line Analytical Systems [PCD 3: Petroleum, Lubricants and their Related Products]

"ज्ञान से एक नये भारत का निर्माण"
Satyanarayan Gangaram Pitroda
"Invent a New India Using Knowledge"

Act Number 22 of 2005
The Indian Parliament
RIGHT TO INFORMATION

Made Available By
Public.Resource.Org

"ज्ञान एक ऐसा खजाना है जो कभी चुराया नहीं जा सकता है"
Bhartṛhari—Nītiśatakam
"Knowledge is such a treasure which cannot be stolen"

BLANK PAGE

BRUTUM FULMEN

IGNORANTIA JURIS NON EXCUSAT

PROTECTED BY COPYRIGHT

IS 15128 : 2002
ISO 10723 : 1995

भारतीय मानक

प्राकृतिक गैस — ऑन-लाइन विश्लेषात्मक पद्धति का कार्यकारिता मूल्यांकन

Indian Standard

NATURAL GAS — PERFORMANCE EVALUATION FOR ON-LINE ANALYTICAL SYSTEMS

ICS 75.060

© BIS 2002

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

May 2002

Price Group 13

Natural Gas Sectional Committee, PCD 24

NATIONAL FOREWORD

This Indian Standard which is identical with ISO 10723 : 1995 'Natural gas — Performance evaluation for on-line analytical systems' issued by the International Organization for Standardization was adopted by the Bureau of Indian Standards on the recommendation of the Natural Gas Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

The text of ISO Standard has been proposed to be approved as suitable for publication as Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'.

b) Comma (,) has been used as a decimal marker while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

Technical Corrigendum 1 to the above International Standard has been printed at the end.

In this adopted standard, reference appears to certain International Standards for which Indian Standards also exist. The corresponding Indian Standards, which are to be substituted in their place, are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 6142 : 1981 Gas analysis — Preparation of calibration gas mixtures — Weighing methods	Nil	—
ISO 6974 : 1984 Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C_8 — Gas chromatographic method	Nil	—
ISO 6976 : 1995 Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition	IS 14504 : 1998 Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition	Identical
ISO 7504 : 1984 Gas analysis — Vocabulary	Nil	—

The Technical Committee responsible for the preparation of this standard will review the provision of ISO 6142, ISO 6974 and ISO 7504 and will decide whether they are acceptable for use in conjunction with this standard.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Contents

Page

1 Scope 1

2 Normative references 1

3 Principle 2

4 Suitability of analytical systems 2

5 Test gases 3

5.1 Definition 3

5.2 Test gas compositions 4

6 Test procedures 5

6.1 System efficiency test 5

6.2 Repeatability 6

6.3 Response concentration relationship 9

6.4 Component separation/interference 13

7 Evaluation of results 14

7.1 System efficiency 14

7.2 Repeatability 14

7.3 Response/concentration relationship 14

7.4 Component separation/interference 15

7.5 Further testing and evaluation 15

Annexes

A Example of application using chromatography 16

B Statistical tests and methods 31

C Bibliography 43

Indian Standard
NATURAL GAS — PERFORMANCE EVALUATION FOR ON-LINE ANALYTICAL SYSTEMS

1 Scope

This International Standard specifies a method of determining whether an analytical system for natural gas is satisfactory, on the assumptions that

a) the analytical requirement has been clearly and unambiguously defined, for the range and uncertainty of component concentration measurements, and the uncertainty of properties which may be calculated from these measurements;

b) the analytical and calibration procedures have been fully described;

c) the method is intended to be applied to gases having compositions which vary over ranges normally found in transmission and distribution networks.

If the performance evaluation shows the system to be unsatisfactory, all the stages, such as

- the analytical requirement;
- the analytical procedure;
- the choice of equipment;
- the choice of calibration gas;
- the calculation procedure;

must be re-examined in the light of the test data to assess where improvements can be obtained.

This International Standard is applicable to analytical systems which give the component concentrations and resulting uncertainties. With the present state of knowledge, the method chosen is likely to be gas chromatography.

Performance evaluation of an analytical system should be performed during installation, then at regular intervals, according to the application, and/or whenever any critical component of the analytical system is changed or replaced.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6142:1981, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6974:1984, *Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C8 — Gas chromatographic method.*

ISO 6976:1995, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition.*

ISO 7504:1984, *Gas analysis — Vocabulary.*

3 Principle

The analytical system is set up according to the instructions so as to carry out the specified compositional analysis. The effectiveness of the system is demonstrated by analysing test gases with compositions covering a range rather wider than that for which the system has been specified.

Test gases prepared according to an appropriate standard are injected into the analyser to test:

a) the ability of the system to measure the components specified in the analytical method (system efficiency);

b) the repeatability of measurement of individual components over their specified ranges;

c) the relationship between response and concentration of individual components over their specified ranges;

d) the absence of interference between components at different concentration ratios.

The tests required for b) and c) above are conducted over intervals of time comparable with the normal period of use between regular calibrations. Because a number of parameters which can influence the analytical performance may vary on a day-to-day basis (barometric pressure variations are a case in point), it is recommended that the tests be repeated on at least three separate intervals, so that occasional inconsistencies may be recognized. However, it is acknowledged that there are circumstances (such as testing analysers installed in remote locations) where only a single set of tests can be obtained.

The results of the tests are analysed to assess analyser performance with respect to bias, repeatability and interference. The repeatability test b) shows the random error associated with the measurement of a component and whether this varies with concentration. The response function c) shows the likelihood of bias error arising from different component concentrations in the calibration standard and sample; bias can also result from component interference d).

Accuracy of measurement is not included in this list, since analytical accuracy is fundamentally and principally controlled by the accuracy with which the calibration gas composition is known. The procedures described in this International Standard allow a judgement as to the ability of the analytical method to provide accurate results if used with an accurate and appropriate calibration gas.

4 Suitability of analytical systems

The analytical system to be evaluated shall satisfy the following criteria.

a) The analytical requirement has been carefully defined, for the range and uncertainty of component concentration measurement, or of physical or chemical property calculation, or of both.

b) The analytical and calibration procedures, whether manual or automated, laboratory or process, have been fully described, preferably following appropriate interlaboratory testing. Changes in details of the method are not permissible during the series of tests. If, at the end of the tests, it is clear that the method fails to provide the desired performance, it shall be modified suitably and the entire test procedure reapplied.

c) The method is not intended to be applied to gases having composition or physical or chemical properties that vary over a wider range than would be acceptable for mixing into a normal transmission or distribution system. Thus, in practical terms, it is unlikely that the concentration will vary for an individual component by more than a factor of 20, and the variation for most components is likely to be less than a factor of 10.

d) The analytical system shall be capable of measuring, either individually or in groups, all components which are significant for the analytical requirement. Thus, for the measurement of calorific value, nitrogen, carbon dioxide, individual hydrocarbons from C_1 to C_5 and a composite C_{6+} are commonly required.

NOTE 1 When a number of hydrocarbons are identified and quantified as a group or groups, either the total is reported as though the group extends from the lowest carbon number of that group (e.g. C_{6+}, which indicates all hydrocarbons of carbon number 6 and above), or separate groups may be reported as the total of each carbon number (e.g. total C_6, total C_7, etc.), or further broken down to component types (e.g. C_6 alkanes, as distinct from benzene and C_6 cycloalkanes or naphthenes).

5 Test gases

5.1 Definition

Test gases are mixtures which are used to evaluate the response of the analyser to individual natural gas components, so that the measured response can be compared with the assumed one. They may be multi-component or binary mixtures. In all cases, the matrix gas shall be methane, so that the behaviour of the test gases is as similar as possible to that of natural gases. Binary mixtures can be prepared with smaller uncertainties than multi-component ones, but more mixtures must be made, one set for each non-methane component to be tested. Multi-component mixtures allow more repeats to be performed for each component/concentration combination.

Obviously, similar mixtures can be used to define the response functions of an analyser when it is initially installed, in which case they shall be referred to as range calibration gases.

NOTE 2 The analytical method may require that the response functions be defined upon installation, or, in the absence of such a requirement, the user may choose to establish them. Alternatively, the user may rely on the supplier's or manufacturer's assumptions about response function, which is usually that the response to all components is represented by a straight line through the origin. This latter approach is not likely to take full advantage of the potential accuracy of the method.

There is, of course, no point in defining a more complex response function if the data handling system available with the analyser will not fit response data to such a function.

Having used range calibration gases at a particular time (for example, on Day 1) to define the response, y_i, of a component i in terms of its concentration, x_i, as:

$$y_i = g_i(x_i)$$

subsequent analyses allow the concentrations of unknown samples to be calculated as

$$x_i = g_i^{-1}(y_i)$$

Rather than redefine the instrument response to each component for each new period of use, the assumption is usually made that each response function, g_i, remains broadly unchanged, but that it needs the minor adjustment of a scaling, or calibration factor, which is derived from the regular use of a single calibration gas. This single calibration gas would invariably be a multi-component mixture, chosen to have similar component concentrations to those anticipated in the unknowns. The scaling or calibration factor, a, is defined as

$$a_{ij} = \frac{\text{Response to component } i \text{ in single calibration gas on Day 1}}{\text{Response to component } i \text{ in single calibration gas on Day } j}$$

and the concentrations of the unknowns are calculated as

$$x_i = g_i^{-1}(a_{ij} \cdot y_i)$$

The frequency with which the single calibration gas needs to be used is a matter of experience, and instead of Day 1, we could refer to Hour 1 or Week 1 or Month 1. This frequency shall be defined as part of the analytical method.

The frequency with which the response function, g, if measured by the user, needs to be re-established will be found by applying these test procedures.

From the above, it can be seen that test gases and range calibration gases could be very similar, if not the same, mixtures. When referred to as test gases in this International Standard, they are used to define the up-to-date response function, f, which is then compared with the previously established or the assumed function g.

5.2 Test gas compositions

Test gases shall be chosen to be suitable for the intended application. However, it is not practicable to make up test gases which contain all the components in natural gas, given the complexity of the higher hydrocarbons which are commonly found, and the difficulty of preparing high quality mixtures containing condensible components. Neither can grouped components, such as C_{6+} or total C_7 be used. It is therefore common to use test gases which contain only the major components; nitrogen, carbon dioxide, methane, ethane, propane and butane are commonly used, but any component expected to be present in a concentration greater than 1 % should be included.

Helium, C_5 and heavier hydrocarbons are usually present at such low concentrations that non-linearity of response is unlikely to be a problem. Their repeatability of measurement can be tested using real natural gases, ideally with a range of concentrations appropriate to the application.

The response/concentration relationship shall be tested over the range specified for each component present in the test gases, and ideally over a slightly greater range. It is unlikely that a response function more complex than a third-order polynomial will be useful and this is satisfactorily defined with seven points. In those instances where the range specified for a component is relatively large, it is possible that the repeatability may vary across the range. For this reason, repeatability testing is carried out with the same mixtures that are used to evaluate the response/concentration relationship.

It is rare that an analyser, however well configured, will measure the sum of components in a natural gas to be exactly 100 %. Consequently, it is common for analysers which have been set up for natural gas analysis to normalize the composition data to 100 %, or to some slightly lesser value if there is a small, constant and recognized contribution from an unmeasured component such as helium. This is based on the obvious premise that a natural gas contains 100 % of components, and not some other value. The method should quote limits within which such normalization would be acceptable; a measured total of between 99 % and 101 % may be deemed to be usual, with analyses producing wider-ranging totals being rejected. Analytical methods which calculate the methane by difference do not normalize in this way, but instead force the total to 100 %, with the calculated methane value absorbing the errors in all the other component measurements.

Repeatability is influenced by the normalization procedure; normalized data are usually significantly more precise than unnormalized data. At the same time, normalization allocates the errors involved in the fact that the total does not reach 100 % or thereabouts between the components *pro rata*. If the error is produced mainly by one component (for example, methane), the normalization process slightly increases the errors for all other components. This shall be recognized in the procedure. Simplistically, there are two types of error which contribute to totals other than 100 %, and hence to the need to normalize. The first type affects all components to the same extent, and in the case of a gas analyser is typically caused by, among other influences, variations in sample pressure within the sample introduction device. The second type affects components to a different extent, and could be for example due to random noise, or to variations between the measured and assumed response functions for individual components.

The first type can be compensated for by normalization, but not the second. Furthermore, normalization takes account of the total calculated composition, according to the equation

$$\text{Unnormalized total} = \sum_{i=1}^{i=n} x_i = \sum_{i=1}^{i=n} g_i^{-1}(a_{ij} \cdot y_i)$$

Consequently, while it might be interesting to use normalized calculated data, or to normalize raw instrument-response data according to the calculated unnormalised total, this requires assumptions about the response function, g_i, and the short-term calibration factor, a_{ij}, which are unlikely to be justified at this stage. The test gases should be used in circumstances which minimize errors of the first type, such as shutting off the sample flow before introduction of the sample. Only unnormalized data should be used for these tests.

Each component shall be tested at seven values of concentration. These shall be, so far as possible, equally spaced across the specified range, and also covering one point below and one point above the range. If the lowest and highest concentrations specified are x_L % and x_u %, the mixtures should contain:

Mixture	**Concentration** (%)
1	$x_L - 0{,}25\ (x_u - x_L)$
2	x_L
3	$x_L + 0{,}25\ (x_u - x_L)$
4	$x_L + 0{,}5\ (x_u - x_L)$
5	$x_L + 0{,}75\ (x_u - x_L)$
6	x_u
7	$x_u + 0{,}25\ (x_u - x_L)$

Achieving these exact values may not always be possible, in which case the nearest practicable concentration should be the aim. Thus if $x_L = 1$ and $x_u = 10$, the concentration value for mixture 1 would be negative, and so a value of $(0{,}5x_L)$ % may be chosen. If $x_L = 0$, mixture 1 may be chosen to be near the limit of detection, and mixture 2 to be between this value and mixture 3. Similar problems may occur for methane. The uncertainty with which these target concentrations are met should be not greater than $\pm\ 0{,}1\ (x_u - x_L)$ %. The uncertainty relating to knowledge of the exact concentrations achieved should, of course, be significantly smaller than this.

Where multi-component mixtures are to be used, it is unlikely that each one can be formulated to have a composition similar to that of an anticipated sample gas, and particular mixtures may contain more propane than ethane, for example. However methane will always be the major component.

These mixtures shall be prepared or certified by a method whose overall uncertainty is not greater than that specified for the analytical system under test, and preferably rather less.

6 Test procedures

6.1 System efficiency test

The analytical system shall be capable of measuring each component for which the method has been specified, over the expected range of concentrations. It shall not give false indications for any other components not specified in the analytical requirement, but which may reasonably be expected to be occasional contaminants in a sample. Furthermore, the system should not give any response for specified components in their absence.

The ability of the method to cope with the specified components shall be assessed by analysis of standard gases which have been prepared to contain these components at appropriate levels, or of natural gases the compositions of which have been defined by comparison with such standards. Exact quantitative accuracy is not needed here, so the methods of preparation may be selected for speed or convenience.

If the method is configured in such a way that one or more groups of components are measured as a single "pseudo-component" or series of "pseudo-components", the correct allocation of components to these groups shall be checked. A typical example would be a recombined (e.g. backflushed) C_{6+} group, consisting of all C_6 and heavier hydrocarbons. The timing of the backflushing operation shall not allow any C_6 or heavier components to fail to be included, nor C_5 or lighter components to be grouped where they should not be.

The approach to the presence of contaminants in a sample will vary according to whether or not remedial action is required. Air is a common contaminant if samples are taken for laboratory analysis, and can be recognized by the presence of oxygen. Usually, an analytical method will permit the composition to be recalculated on an air-free basis, provided that the concentration of air is below a defined value. In this case, the oxygen shall be measured with high accuracy, since the adjustment for a given observed amount of oxygen involves the removal of a calculated amount of nitrogen which is about four times larger. On the other hand, in particular circumstances other components may be expected to be present at concentrations comparable to those of the C_4 or C_5 hydrocarbons, but their measurement is not required for the purpose for which the analysis is performed. In this case, it shall be established whether or not the contaminant interferes with measurement of any of the expected components, and if so, how large an effect is seen.

Any response for a component in its absence can be tested by a blank experiment, which simulates all the activities of the analytical system. Thus, in the case of a chromatographic method, injection of carrier gas instead of sample gas would be appropriate.

Any detectable response at this stage should, if possible, be eliminated by suitable adjustment of the method. Otherwise, it will impose a fixed bias error on the response/concentration relationship.

6.2 Repeatability

Repeatability is often measured as that of instrument response; the standard deviation of peak area counts in the case of a chromatographic method. This measurement cannot be used in isolation for two reasons. The mean and standard deviation of a normally distributed (Gaussian) set of data are measures such that 67 % of all the data points lie within ± 1 standard deviation of the mean; thus, while the standard deviation is a convenient measure to use while assessing error contributions, it shall be converted at the end of the calculations to a value which more nearly describes what we understand by repeatability (see clause B.4). Also, a typical analytical result is derived using a relationship of the type

$$x_{\mathrm{s}} = \frac{\mathrm{s}}{y_{\mathrm{std}}} \times x_{\mathrm{std}}$$

where

x_{s} is the concentration in unknown (sample);

y_{s} is the response to unknown (sample);

x_{std} is the response to standard;

y_{std} is the concentration in standard.

Consequently, the repeatability of the result is influenced by the repeatability of both the unknown and of the standard. Uncertainty associated with the calibration gas standard also contributes, but is outside the scope of this International Standard. The evaluation procedure assesses the ability of the analytical system to provide high quality data, if used with a calibration standard which has a well-known composition and is appropriate for the application. The quality of such calibration standards is properly dealt with in other International Standards.

The repeatability of measurement of a component may be uniform over the expected concentration range, or it may vary as a function of concentration. Figure 1 illustrates the former situation, where the Gaussian curves superimposed on the response/concentration plot represent the repeatability distribution, which can be seen to be uniform across the range.

Figure 2 shows a plot where the repeatability increases with concentration. The likelihood of any particular measurement point deviating from the plotted line is indicated by the width of the Gaussian curve in that region.

The difference between these forms of behaviour is important, so that the repeatability for different components at different concentrations may be expressed appropriately.

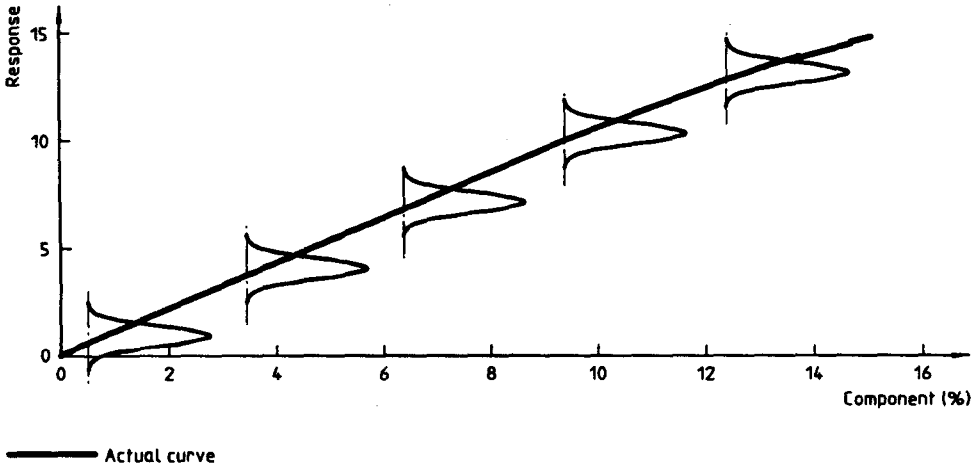

Figure 1 — Uniform repeatability

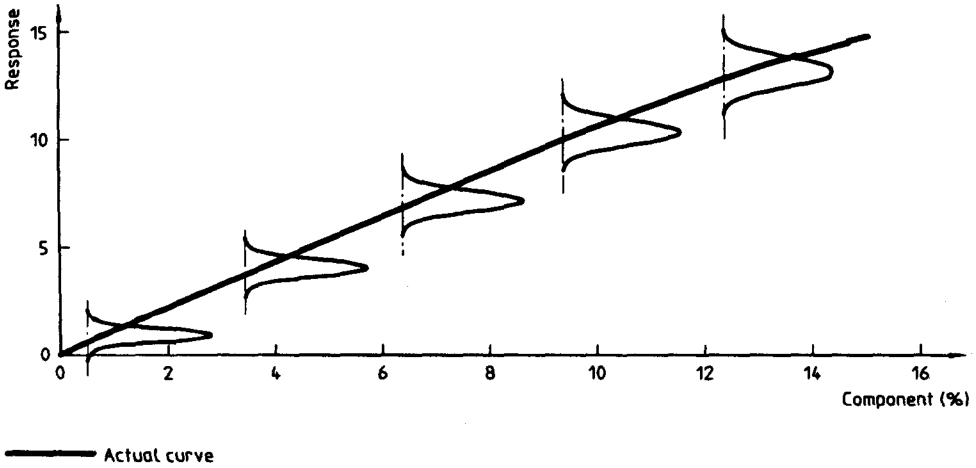

Figure 2 — Variable repeatability

6.2.1 Calibration interval

For the purpose of this test, the calibration interval is defined as that period of time during which the analytical system would normally be used between recalibrations. Experience will show over how long a period an instrument may be judged to be stable, and hence what the recalibration frequency should be. A laboratory instrument may be used throughout the working day after having been calibrated first thing in the morning, or may require separate calibrations for the morning and afternoon. A process analyser may operate for 24 h a day with automatic recalibration at midnight. It is important that one set of tests is conducted within one calibration interval and that they are spaced uniformly throughout it. The longer the calibration period, the longer the time for one set of tests.

6.2.2 Procedure

Calculate the number of analyses that can be performed within the calibration interval and then analyse the seven concentration levels, using a random sequence, as many times as possible. Five repeats at each level will usually give statistically useful data. (It is hardly practicable to exceed 10 repeats at each level: this implies 10 x 7 = 70 analyses during the calibration interval.)

Where possible, repeat this set of tests so as to have at least three sets of results, each achieved during a different calibration interval.

For each of e components ($i = [1, ..., e]$), at each of seven concentration levels ($j = [1, ..., 7]$), perform f repeat analyses ($k = [1, ..., f]$) during each of g calibration intervals ($l = [1, ..., g]$). Record each analyser response, y_{ijkl}, together with the component concentration, x_{ij}, which generated it.

Group the results by component and level from within one calibration interval, y_{ij11}, y_{ij21}, etc. Inspect each group for outliers or stragglers using Grubbs' test or some other suitable outlier test (see annex B). After rejection of any outliers, calculate the means, y_{ij1}, standard deviations, s_{ij1}, and adjusted numbers of analyses, n_{ij1}.

Where tests have been performed during different calibration intervals, compare the precision of sets of results between the calibration intervals s_{ij1}, s_{ij2}, ..., s_{ijg}, by Cochran's test (see annex B). If any group of results is shown to be significantly less precise than the others, the reason for this shall be investigated. In the absence of a clear reason, and one which would be expected to be evident in normal use, the tests shall be repeated.

Assuming that each component at each level shows uniform precision between the calibration intervals, a combined mean and standard deviation can be derived. The mean, y_{ij}, is calculated as

$$y_{ij} = \frac{\sum_{l=1}^{l=g} y_{ijl} \cdot n_{ijl}}{\sum_{l=1}^{l=g} n_{ijl}}$$

The combined standard deviation, s_{ij}, is calculated as

$$s_{ij} = \left[\frac{\sum_{l=1}^{l=g} (n_{ijl} - 1) \cdot (s_{ijl})^2}{\sum_{l=1}^{l=g} n_{ijl} - 1} \right]^{1/2}$$

If, in the examination of error structure (see 6.3.1), the standard deviation, s_{ij}, appears to be independent of the concentration, x_{ij}, a combined standard deviation, s_i, covering the full concentration range for component i, can be calculated from the standard deviations at each level, s_{ij}, and the total number of measurements at each level across all the calibration intervals, n_{ij}:

$$s_i = \left[\frac{\sum_{j=1}^{j=7} (n_{ij} - 1) \cdot (s_{ij})^2}{\sum_{j=1}^{j=7} n_{ij} - 1} \right]^{\frac{1}{2}}$$

If there is a dependence of standard deviation on concentration, it can be expressed as

$$s_i = a + b \cdot x_i$$

or

$$s_i = a + b \cdot x_i + c \cdot x_i^2$$

or

$$s_i = a + b \cdot x_i + c \cdot x_i^2 + d \cdot x_i^3$$

where a, b, c and d are the coefficients of linear regression of s_{ij} on x_{ij}. The indication as to which polynomial to use is made in the same way as for the response/concentration relationship described below. The choice of polynomial should take into account this indication, but also a reasonable interpretation of how the standard deviation might be expected to vary with concentration. A second-order polynomial can, within the range tested, contain a maximum or a minimum; a third-order can contain both. If such a maximum or minimum is seen, the higher order polynomial should be rejected if it is reasonable to assume that the relationship should be monotonic, i.e. continuously increasing or decreasing, though not necessarily following a straight line.

The standard deviation, $s(x_i)$, of the amount of a component, x_i, is calculated from the standard deviations of the responses due to that component from the sample and from the standard, using the equation

$$\left[\frac{s(x_i)}{x_i}\right]^2 = \left[\frac{s(y_{is})}{y_{is}}\right]^2 + \left[\frac{s(y_{i\text{std}})}{y_{i\text{std}}}\right]^2$$

where

y_{is} and $y_{i\text{std}}$ are the instrument responses to component i in the sample and standard;

$s(y_{is})$ and $s(y_{i\text{std}})$ are the respective standard deviations.

Standard deviations of component amount are calculated for a number of gas compositions across the anticipated range. The rigorous way of calculating the repeatability of component measurement, $r(x_i)$, is

$$r(x_i) = t\sqrt{2}\, s(x_i)$$

where

t is taken from the two-sided t-table at the 5 % level with the number of degrees of freedom appropriate to whether the standard deviation has been found to be uniform ($= \sum_j n_{ij} - 1$) or a function of concentration ($= \sum_l n_{ijl} - 1$);

$\sqrt{2}$ reflects the fact that repeatability is the difference between two single measurements.

However, the confidence interval for the standard deviation is likely to be so wide that such nice distinctions are unjustified, and the repeatability can in all cases be expressed as

$$r(x_i) = 2{,}8 s(x_i)$$

Compare the repeatability of measurement for each component with the analytical requirement.

6.3 Response concentration relationship

Use of the test gases defines the relationship between the concentration of a component, x_i, and the response to it, y_i, as

$$y_i = f_i(x_i)$$

This relationship can then be used to calculate the concentration of component in a sample, x_i, within the range tested using the equation

$$x_i = f_i^{-1}(y_i)$$

If, in fact, the analytical system assumes that a different response characteristic, for example $y_i = g_i(x_i)$, is obtained, an error will be introduced which depends on the difference between the functions f_i and g_i, and on the difference in concentration of component i between calibration gas and sample.

The scale of the direct measurement error may be calculated using the equation

$$\varepsilon_i = g_i^{-1}\left[\frac{g_i(x_{i\mathrm{std}})\cdot f_i(x_{is})}{f_i(x_{i\mathrm{std}})}\right] - x_{is}$$

and therefore can be seen to tend towards zero either as the amounts of component in the standard and sample converge ($x_{is} \rightarrow x_{i\mathrm{std}}$), or as functions f_i and g_i converge.

Most analytical systems assume that $g_i(x_i) = \mathrm{constant}\cdot x_i$. This is the equation of a straight-line plot through the origin, and justifies single-point calibration, as only the constant needs to be defined. In this case, the error depends on how close the true response function, $f_i(x_i)$, is to a straight line through the origin, and on the difference between standard and sample concentrations.

This is illustrated in figure 3. The solid line shows a response curve which deviates somewhat from a straight line. The two broken lines are straight lines through the origin, coinciding with the actual curve at 8 % and 15 % respectively. The area between the broken lines shows the area of uncertainty, depending upon whether an 8 % or a 15 % calibration standard is used.

If the resulting error is small by comparison with other variations (e.g. the repeatability), it may be acceptable. Otherwise, the response curve can be used for quantitative purposes, usually in a subsequent data-handling stage. Even this is not completely satisfactory, because to define the shape of the curve is time-consuming, and therefore not likely to be rechecked very frequently. The most satisfactory outcome shall be confirmation of the straight line through the origin.

Regression analysis is applied to the data generated in 6.2.2 from the mixtures containing the seven component levels. A judgement is made as to whether a first-order (i.e. a straight line), second-order, or third-order polynomial represents the "best fit".

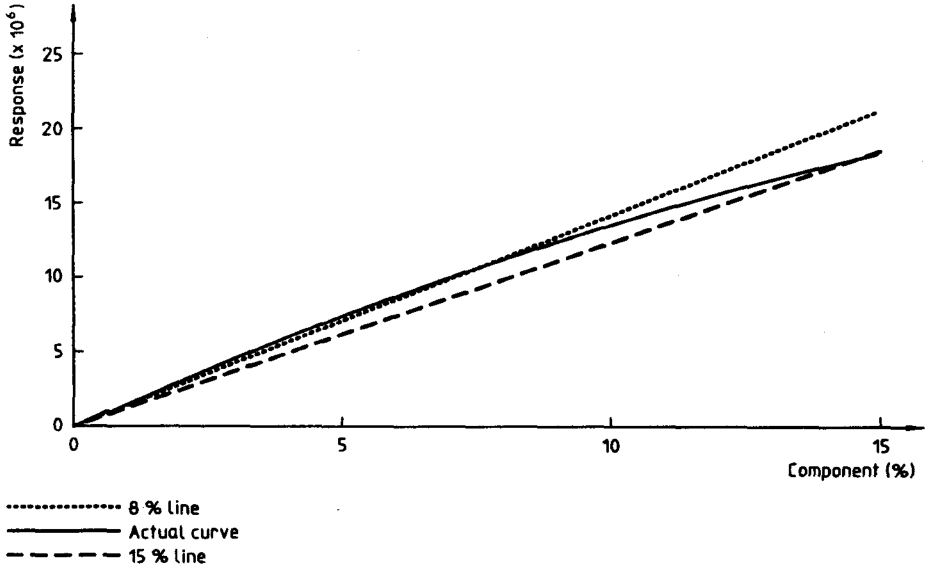

Figure 3 — Response curve/straigth lines

6.3.1 Examination of error structure

Normal regression analysis assumes that errors in measurement

a) are independent;

b) have a zero mean;

c) have a constant variance;

d) are normally distributed.

In analytical methods for natural gas, assumption c) may not always be true. Considering the repeatability error, it is likely to be constant for methane over a range 75 % to 95 %, but may well vary for ethane over a range 1 % to 10 %. Rigorously, the approach to determination of the response function by regression analysis depends upon whether the errors are constant or vary across the range, and consequently whether the data should be used directly or weighted. In fact, the equation of the line is influenced only marginally according to whether weighted or unweighted regression is used; the difference shows in the associated uncertainties when values are calculated from the regression equation. Only the equation of the response function is required in this subclause, and so weighting of data is not necessary.

6.3.2 Regression analysis

The aim is to decide whether the relationship between response and concentration of a component is best described by a polynomial function of

— first order

$$y_i = a + b \cdot x_i$$

or

— second order

$$y_i = a + b \cdot x_i + c \cdot x_i^2$$

or

— third order

$$y_i = a + b \cdot x_i + c \cdot x_i^2 + d \cdot x_i^3$$

(If none of these functions gives a good fit to the data, then the instrument response is more complex than would normally be considered to be useful for accurate analysis. Although complicated response characteristics can be accounted for by a good data system, system accuracy inevitably deteriorates with increasingly complex algorithms.)

Two procedures are described in annex B, orthogonal polynomials and backwards elimination by the sequential F-test. Orthogonal polynomials differ from conventional polynomials (as above) in that the coefficients describe the mean height or centre of gravity of the x data, the mean slope of the line, the mean curvature, etc. The coefficients are therefore independent of each other, and can be tested simultaneously. The sequential F-test uses data from an ANalysis Of VAriance (ANOVA) table, and tests each highest conventional coefficient in turn to judge whether it offers a more significant improvement in fit than the polynomial of the next lower order.

6.3.3 Scale of error

Any error resulting from the concentration/response relationship will be a bias which depends, as described above, upon the difference between the measured relationship and that assumed as part of the analytical method, and upon the difference between component concentrations in the standard and sample. If the method requires that the results be normalized, a further error will be introduced as a result of this procedure.

The significance of this depends on the analytical procedure and on the component. If the only component displaying bias error is methane, the effect of normalization is to remove most of this error. This is not likely to be the case for other components, and the effect on their final value depends both on their own bias and on that for methane.

For each component, i, the response has been shown to be of the form $y_i = f_i(x_i)$, where the function f is a first-, second- or third-order polynomial. This is the "true" response function. A different response function, $y_i = g_i(x_i)$, may be claimed by the supplier of the analyser, or have been established in a previous evaluation. In the absence of any such information, the function may be taken to be of the form $y_i = \text{constant} \cdot x_i$, which is the equation of a straight line through the origin; the constant may be assumed, initially at least, to have the value b, the polynomial coefficient of x_i.

Consider particular values for component concentrations in a standard and a sample, $x_{i\text{std}}$ and $x_{i\text{s}}$. These are likely to be the preferred or recommended value for the standard, and one extreme of sample composition. The "true" and assumed responses of the calibration standard, $y\text{t}_{i\text{std}}$ and $y\text{a}_{i\text{std}}$, would be

$$y\text{t}_{i\text{std}} = f_i(x_{i\text{std}})$$

$$y\text{a}_{i\text{std}} = g_i(x_{i\text{std}})$$

In fact, with single point calibration, the only information available is the concentration of and response to the standard. Two different responses for the standard are not possible, so a coefficient, k_i, is calculated such that

$$\begin{aligned} f_i(x_{i\text{std}}) &= k_i \cdot g_i(x_{i\text{std}}) \\ &= y\text{t}_{i\text{std}} \end{aligned}$$

The coefficient, k_i, performs the regular calibration role of relating response to concentration at the value of the standard.

The assumption is now made that this relationship extends to the sample, i.e.

$$y_{i\text{s}} = k_i \cdot g_i(x_{i\text{s}})$$

and so the sample concentration, $x'_{i\text{s}}$, is calculated as

$$x'_{i\text{s}} = g_i^{-1}\left(k_i^{-1} \cdot y_{i\text{s}}\right)$$

$$x'_{i\text{s}} = g_i^{-1}\left[\frac{g_i(x_{i\text{std}}) \cdot f_i(x_{i\text{s}})}{f_i(x_{i\text{std}})}\right]$$

For each component present in the test gases, set $x_{i\text{s}}$ in turn to the lowest and highest value anticipated by the method, and $x_{i\text{std}}$ to the recommended value for the calibration gas. Calculate $x_{i\text{s}}$ and the error $\varepsilon_i = x'_{i\text{s}} - x_{i\text{s}}$.

NOTE 3 The inverse g^{-1} of the function g cannot always be found. In the case of a first-order polynomial

$$y = a + bx$$

the inverse is

$$x = \frac{y - a}{b}$$

For a second-order polynomial

$$y = a + bx + cx^2$$

the inverse is

$$x = \frac{-b \pm \sqrt{b^2 - 4(a - y)c}}{2c}$$

to which one of the solutions will fall within the range of interest. (If both solutions fall within the range, the response function shows a maximum or a minimum within the working range in such a way as to be unusable.)

A third-order polynomial

$$y = a + bx + cx^2 + dx^3$$

does not permit generalized derivation of an inverse. However, individual values of x can be found by iterative numerical analysis. Obviously, a single value of y allows three possible values of x, and so the routine should be constrained so that the solution is within the expected range of x (i.e. the concentration range of the component).

If the results are to be normalized, total compositions shall be postulated. The worst case is likely to be found if all of the non-methane components are set at their lowest level in one case, and at their highest in the other. It follows that the methane content of the first mixture will be at or near its highest value, and vice versa for the second. Consider each of these mixtures in turn, with reference to the suggested calibration standard. Calculate x'_{is} for each of the m components, using x_{istd} from the calibration standard, x_{is} from the mixture, and the known and assumed functions f_i and g_i. (Components present at a low level, such as helium and C_5 and higher hydrocarbons, which have not been tested for response characteristics, may be assumed to be not subject to bias error, but should be included in these compositions.)

Calculate the unnormalized total in each case using

$$x_t = \sum_{i=1}^{i=m} x'_{is}$$

and then the normalized component concentrations as

$$x''_{is} = \frac{100x'_{is}}{x_t}$$

The error resulting is $x''_{is} - x_{is}$.

6.4 Component separation/interference

Where a chromatographic method describes a required degree of resolution between particular pairs of peaks, this can be measured from the chromatogram, using the method defined in ISO 7504:1994, 3.3.4.2. Alternatively, it can be calculated from peak area and height data, and retention times. Provided that the time base of the integrator or data system is known, the peak width at half-height can be derived by dividing peak area (expressed as the product of instantaneous detector signal and time base units) by peak height. This value can be converted to the width at the peak base by multiplying by 4, and dividing by $\sqrt{2 \ln 2}$.

If peak resolution is not specified in the analytical method, 6.4.1 indicates acceptable levels of separation between components based on common methods of measuring the performance of chromatographic analysers. If measurement criteria are not met, or if these measurements are not appropriate, 6.4.2 describes direct measurement of interferences.

6.4.1 For symmetrical peaks approximating to a Gaussian shape, the areas of which are measured, interference from adjacent components is not likely if the resolution between the peaks is greater than or equal to 1,75, as defined in ISO 7504:1984, 3.3.4.2.

Components whose properties are virtually identical as judged by the purpose for which the analysis is being performed, for example *i*-butane and *n*-butane where calorific value or relative density is to be calculated, may be measured with a resolution between them of not less than 1,25.

Any component which is present at a concentration of less than 0,01 % molar can be measured with a separation of not less than 1,25 between itself and adjacent larger components provided that the ratio between the signals due to the components is not greater than 50:1.

Where adjacent components are to be summed as part of a group for the purposes of the analysis, there is no requirement for a minimum separation between them.

In all other circumstances, or if there is evidence of peak asymmetry, such that adjacent peaks may interfere with each other, the scale of such interference shall be measured as described in 6.4.2.

6.4.2 If the ratio of signal sizes between a pair of components which are suspected of mutual interference is greater than 2:1, measure the effect of the component which gives the smaller signal only, otherwise, measure the effect on both.

Using gas mixtures prepared according to ISO 6142, inject samples containing the following compositions:

Mixture	Major component	Minor component
1	Expected concentration + 50 % (± 5 % relative value)	Expected concentration (± 5 % relative value)
2	Expected concentration (± 5 % relative value)	Expected concentration (± 5 % relative value)
3	Expected concentration – 50 % (± 5 % relative value)	Expected concentration (± 5 % relative value)

Unless the major component is methane, the gases should be prepared using methane as the complement gas. The ± 5 % relative value indicates the tolerance with which the target values would be expected to be met. The uncertainty on the actual concentration would be that associated with the method of preparation.

Using mixture 2 as the standard, the measured values for the minor component in mixtures 1 and 3 are compared with the known concentrations. The measured and known concentrations should not differ in each instance by more than the measured method repeatability for that component.

7 Evaluation of results

7.1 System efficiency

This is obviously the most fundamental test. Failure at this stage would indicate that the wrong analytical method has been selected. Apparent response in the absence of a component (a "blank" run) may be curable with detailed knowledge of the method. In the case of a chromatographic method, it may be possible to adjust valve switching times or to clean up the carrier gas to achieve better results.

7.2 Repeatability

The method repeatability shall be satisfactory before any other tests can be usefully applied. If the desired values are not met, it may be possible to improve the control aspects of the analytical method, such as the sample introduction procedure, or to reduce the calibration interval so that uniformity of results is required over a shorter period of time. In the latter case, there is a change to the analytical requirement, which shall be acceptable.

If measures such as these are not effective, another analytical method shall be selected.

7.3 Response/concentration relationship

Ideally, the bias error caused by the difference between the observed and the assumed response of the method should be small by comparison with the repeatability. If, however, the repeatability error is small by comparison with the analytical requirement, the bias error may represent most of the overall error, and should be assessed accordingly.

If the bias errors are unacceptably large, it may be possible to tailor the method so as to make them reasonable. In the case of a chromatographic method, reducing the size of the injected sample will generally cause the response to be a more nearly linear function of concentration.

Another significant influence on the bias error is the difference in component concentrations between the standard and sample. If the change in the analytical requirement is tolerable, it is possible to calculate from the data how closely the standard and sample should be to each other so that the resulting bias error is acceptably low. This will require that more standard gases are used to cover the range of component concentrations required.

7.4 Component separation/interference

Failure of the system to achieve the required freedom from interference, whether evaluated ba analysis of potentially interfering gas mixtures or inferred from measurement of an output signal such as a chromatogram, means that a new or modified analytical system must be found.

Again, it may be possible to assess from the data how this could be achieved. In the case of a chromatographic method, it may be possible to optimize carrier gas flowrate or adjust the column temperature to improve separation and hence reduce interference.

7.5 Further testing and evaluation

If the analytical method is changed as a result of the evaluation described in 7.1 to 7.4, it shall be regarded as a new method, however apparently small the changes may seem.

This new method shall be subjected to the entire procedure of testing and evaluation as described in clause 6 and in 7.1 to 7.4, before being accepted as satisfying the analytical requirements.

Annex A
(informative)

Example of application using chromatography

A.1 Analytical requirement

A compositional analysis of natural gas is required, from which the calorific value and relative density may be calculated using the method described in ISO 6976. Components to be measured include nitrogen, carbon dioxide and all saturated hydrocarbons in the range C_1 to C_5. Components heavier than C_5 may be measured individually, or as a composite "pseudo-component", referred to as C_{6+}. If these components are measured individually, they will be summed after the analysis to a C_{6+} value. The helium content is assumed to vary so little that it need not be analysed, but a constant value is taken.

The allowable uncertainty of measurement of individual components is related to the concentration. The maximum uncertainty ε_{x_i}, expressed as relative percentage, is, as a function of component concentration, x_i, expressed in percentage molar:

$$\frac{\varepsilon_{x_i}}{x_i} = 1,5\left(x_i^{-0,45}\right)$$

(This equation describes the relative uncertainty/concentration relationship as a continuous function across the range.)

The method is to be applied to components in the following ranges:

Nitrogen	1 % to 12 %
Carbon dioxide	0,1 % to 1 %
Methane	80 % to 95 %
Ethane	1 % to 7 %
Propane	0,1 % to 2 %
i-Butane	0,04 % to 0,35 %
n-Butane	0,04 % to 0,35 %
Neopentane	0,002 % to 0,01 %
i-Pentane	0,01 % to 0,06 %
n-Pentane	0,01 % to 0,06 %
Hexanes+	0,1 % to 0,4 %

The allowable uncertainties on composition will therefore be, for the lower levels:

Component	**Level**	**Relative uncertainty** (%)	**Absolute uncertainty**
Nitrogen	1,0	1,5	0,015
Carbon dioxide	0,1	4,2	0,004
Methane	80,0	0,21	0,17
Ethane	1,0	1,5	0,015
Propane	0,1	4,3	0,004
Butanes	0,04	6,4	0,002 6
Neopentane	0,002	24,6	0,000 5
Pentanes	0,01	11,9	0,001 2
Hexanes+	0,1	4,2	0,004

and for the upper levels:

Component	**Level**	**Relative uncertainty (%)**	**Absolute uncertainty**
Nitrogen	12,0	0,49	0,059
Carbon dioxide	1,0	1,5	0,015
Methane	95,0	0,19	0,18
Ethane	7,0	0,62	0,044
Propane	2,0	1,1	0,022
Butanes	0,35	2,4	0,008
Neopentane	0,01	11,9	0,001 2
Pentanes	0,06	5,3	0,003 2
Hexanes+	0,4	2,3	0,009

The calculated calorific value and relative density have a maximum allowable uncertainty of 0,2 % relative.

A.2 Description of method

The analytical method is designed for measurement of nitrogen, carbon dioxide, methane, ethane, propane, two butanes, three pentanes and total hexanes+ in natural gas. The method is intended for on-line use, and does not distinguish oxygen from nitrogen.

The method uses gas chromatography with a thermal-conductivity detector and helium carrier gas. A boiling-point column is used for propane and heavier hydrocarbons. A switching valve diverts the lighter components, nitrogen, carbon dioxide, methane and ethane onto a porous polymer bead column where they are stored and analysed later in the cycle. The boiling-point column is divided into two sections, with the shorter pre-section used for rapid backflush of hexanes+ to the detector. A typical chromatogram is shown in figure A.1.

Calibration is performed using a single calibration mixture at 24 h intervals, and the data handling assumes that the shape of the response curve for each component is a straight line through the origin. The composition of the calibration gas is chosen to be intermediate between the extreme levels of concentrations. The uncertainty on its composition, expressed as a standard deviation, is given below.

Component	**Concentration**	**Uncertainty**
Nitrogen	6,5	0,004
Carbon dioxide	0,6	0,001
Methane	87,12	0,012
Ethane	4,0	0,003
Propane	1,0	0,001 5
i-Butane	0,20	0,0007
n-Butane	0,20	0,000 8
Neopentane	0,006	0,000 07
i-Pentane	0,04	0,0002
n-Pentane	0,04	0,000 2
Hexanes+	0,25	0,002 8

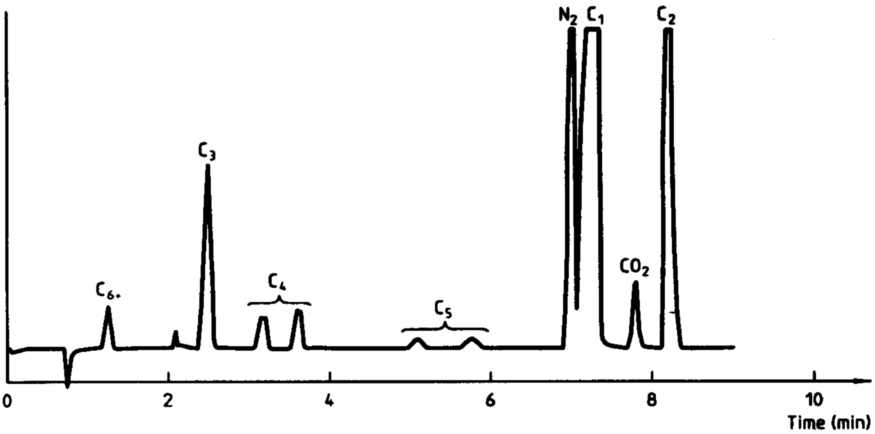

Figure A.1 — Typical chromatogram

A.3 System efficiency test

The appearance of the chromatogram indicates that the method is suitable for the application. It can be seen that the spike caused by the valve switching operation which appears between the C_{6+} and propane peaks does not appear to affect the quantitative measurement of either peak. Injection of pure carrier gas instead of sample gives no false peak indications discernible by the data handling system.

The validity of the C_{6+} peak as representing all hydrocarbons of carbon number 6 and higher, and only those, is checked with a gas mixture containing appropriate concentrations of *n*-pentane, the heaviest component to be measured individually, and 2,2-dimethylbutane, the lightest one to be included in the C_{6+} group. This mixture is injected repeatedly, with the timing of the pre-column backflush reduced in stages of 2 s until the area of the *n*-pentane peak starts to diminish. The timing is reset to the original value, then increased in stages until the area of 2,2-dimethylbutane (as measured by the C_{6+} peak) starts to diminish. The first test ensures that all of the *n*-pentane has passed onto the analytical column before backflushing, and the second that none of the 2,2-dimethylbutane has done so. Satisfactory performance is shown by there being a reasonable and approximately equal margin of tolerance in each direction before the area of either peak is seen to diminish.

A.4 Repeatability and linearity

The pentanes and hexanes+ are present at levels such that non-linearity of response is very unlikely. The two butanes are assumed to have similar behaviour, and so testing for repeatability and linearity is performed with gas mixtures containing nitrogen, carbon dioxide, methane, ethane, propane and *n*-butane. Repeatability data for the pentanes and for hexanes+ are obtained from several analyses of a cylinder of typical natural gas.

A.4.1 Data for one calibration interval

Seven six-component mixtures were prepared containing nitrogen, carbon dioxide, methane, ethane, propane and *n*-butane at levels which span the range described in the analytical requirement. The compositions of these mixtures, which are labelled 301 to 307, are given in table A.1.

Table A.2 gives the area counts for each of six analyses of each of these mixtures.

Table A.1 — Test gas compositions

Mixture No.	Component (%)					
	Nitrogen	Carbon dioxide	Methane	Ethane	Propane	*n*-Butane
301	0,331	0,040	98,557	1,029	0,033	0,011
302	1,019	1,001	95,294	0,272	2,007	0,407
303	2,527	0,540	91,988	3,982	0,793	0,170
304	5,565	0,325	88,195	5,460	0,356	0,099
305	8,022	1,389	85,097	2,547	2,615	0,329
306	11,073	0,099	81,966	6,496	0,114	0,252
307	14,512	0,739	75,296	8,046	1,412	0,041

Table A.2 — Area counts from one calibration interval

	Mixture No.						
	301	302	303	304	305	306	307
	Sequence						
	4	5	2	7	3	1	6
Nitrogen (% molar)	0,331	1,019	2,527	5,565	8,022	11,073	14,512
Area	502 326	1 546 370	3 900 460	8 499 470	12 262 000	16 908 900	21 991 700
	462 328	1 543 020	3 864 380	8 474 400	12 272 300	16 930 100	22 008 600
	455 031	1 544 030	3 859 810	8 478 560	12 271 900	16 913 100	22 000 800
	458 934	1 540 830	3 862 550	8 478 710	12 266 100	16 911 700	21 995 800
	457 211	1 545 380	3 861 520	8 475 130	12 266 600	16 905 900	21 996 100
	458 852	1 538 760	3 856 120	8 478 750	12 267 300	16 914 200	21 989 500
Mean	458 471	1 543 065	3 860 876	8 477 110	12 267 700	16 913 983	21 997 083
Standard deviation	2 676,6	2 854,6	3 132,5	2 157,3	3 878,7	8 449,5	6 863,6
Carbon dioxide (% molar)	0,040	1,001	0,540	0,325	1,389	0,099	0,739
Area	79 182	1 799 930	973 170	583 572	2 471 030	181 206	1 352 930
	69 768	1 799 820	981 912	585 174	2 469 020	178 356	1 342 100
	67 296	1 801 500	978 636	580 860	2 472 440	178 278	1 337 100
	66 924	1 797 200	982 689	583 962	2 471 510	181 560	1 334 570
	70 500	1 805 230	980 754	574 113	2 471 050	180 972	1 336 240
	71 082	1 799 780	979 230	584 052	2 469 710	180 000	1 332 490
Mean	69 114	1 800 577	979 399	581 956	2 470 793	180 062	1 339 238
Standard deviation	1 892,3	2 665,8	3 417,2	4 101,2	1 238,2	1 447,6	7 437,0

Table A.2 *(concluded)*

	Mixture No.						
	301	302	303	304	305	306	307
	Sequence						
	4	5	2	7	3	1	6
Methane (% molar)	98,557	95,294	91,988	88,195	85,097	81,966	75,296
Area	123 441 000	119 752 000	116 024 000	111 426 000	108 187 000	104 785 000	96 530 700
	123 482 000	119 689 000	116 047 000	111 410 000	108 132 000	104 781 000	96 430 500
	123 473 000	119 678 000	116 020 000	111 392 000	108 120 000	104 753 000	96 403 100
	123 446 000	119 652 000	116 007 000	111 409 000	108 069 000	104 749 000	96 386 100
	123 436 000	119 688 000	115 980 000	111 407 000	108 072 000	104 722 000	96 386 100
	123 443 000	119 580 000	115 949 000	111 408 000	108 060 000	104 754 000	96 365 400
Mean	123 456 000	119 673 167	116 004 500	111 408 667	108 106 667	104 757 333	96 416 983
Standard deviation	20 211,4	56 279,4	34 967,1	10 801,2	49 135,2	23 122,9	59 791,9
Ethane (% molar)	1,029	0,272	3,982	5,460	2,547	6,496	8,046
Area	2 225 860	647 058	8 535 580	11 636 400	5 406 210	13 763 100	16 990 700
	2 215 400	644 262	8 532 290	11 612 000	5 404 670	13 784 700	16 995 200
	2 218 500	643 344	8 530 630	11 607 300	5 403 250	13 768 000	16 970 400
	2 209 940	645 996	8 528 020	11 607 000	5 399 710	13 759 600	16 970 400
	2 214 500	645 315	8 512 380	11 596 900	5 407 670	13 770 000	16 981 800
	2 211 800	644 550	8 514 990	11 616 800	5 406 280	13 765 900	16 959 400
Mean	2 214 028	645 088	8 525 648	11 612 733	5 404 632	13 768 550	16 979 767
Standard deviation	3 308,3	1 324,4	9 621,2	13 343,7	2 848,6	8 718,4	13 161,9
Propane (% molar)	0,033	2,007	0,793	0,356	2,615	0,114	1,412
Area	100 950	5 211 040	2 047 070	927 204	6 746 300	283 236	3 685 610
	78 900	5 217 070	2 053 370	919 572	6 754 750	280 026	3 681 480
	75 222	5 220 030	2 051 990	922 734	6 751 870	281 892	3 680 810
	75 246	5 216 780	2 053 640	921 186	6 751 360	280 218	3 681 610
	73 608	5 221 240	2 054 630	922 152	6 755 420	277 692	3 680 110
	73 734	5 206 260	2 052 380	916 752	6 752 150	277 908	3 674 740
Mean	75 342	5 215 403	2 052 180	921 600	6 751 975	280 162	3 680 727
Standard deviation	2 137,5	5 705,9	2 673,5	3 468,6	3 230,9	2 174,6	3 504,9
n-Butane (% molar)	0,011	0,407	0,170	0,099	0,329	0,252	0,041
Area	36 768	1 233 240	522 594	305 886	1 011 530	780 006	127 680
	32 988	1 230 910	524 136	305 286	1 011 890	778 800	125 610
	32 160	1 235 440	522 846	307 038	1 011 390	779 904	123 342
	34 788	1 234 030	521 754	308 628	1 009 080	781 236	122 556
	32 490	1 235 830	521 346	307 860	1 010 470	781 248	123 120
	32 732	1 230 940	522 072	305 520	1 010 810	778 326	122 226
Mean	33 232	1 233 398	522 458	306 703	1 010 862	779 920	124 089
Standard deviation	1 052,4	2 132,6	986,5	1 358,8	1 011,3	1 208,2	2 122,6

A.4.1.1 Repeatability data

Visual inspection of the data (see table A.2) for single outliers shows a number of apparent anomalies. For nitrogen, the first results for mixtures 301, 303 and 304 are all high. For carbon dioxide, the first result for mixture 301 is also high. Methane and ethane appear to show consistent data sets, except that the first result for methane in mixture 307 is slightly high. For propane, the first result from mixture 301 is high, and the first for 303 low. The first result for mixture 301 for butane is also high.

There do not appear to be any data sets with both one high and one low result. Looking for multiple outliers, all high or all low, shows only one potential instance, which is the first two runs for propane in mixture 301.

Applying Grubbs' test for multiple outliers to the data for propane in mixture 301 produces a test value of 1,94, which is less than the critical value (see table B.2) of 2,41 at the 5 % level. Therefore there are not two outliers.

Applying the single outlier test gives the following results:

Nitrogen	301 — first result — outlier (1 % level) 303 — first result — outlier (1 % level) 304 — first result — outlier (1 % level) 306 — second result — straggler (5 % level)
Carbon dioxide	301 — first result — straggler (5 % level)
Methane	307 — first result — straggler (5 % level)
Ethane	No outliers or stragglers
Propane	301 — first result — outlier (1 % level) 303 — first result — straggler (5 % level)
Butane	No outliers or stragglers

The larger number of outliers for nitrogen associated with the first run of each sequence is probably due to a combination of changing from high to low concentrations in the test gases and a small amount of air contamination when changing cylinders. The first run of mixture 301 produced outlier values for nitrogen and propane, and a straggler for carbon dioxide. In view of this, it was decided to eliminate data for all components from this run, even though methane, ethane and butane did not, by themselves, show up as anomalies.

Other than this, the normal procedure of rejecting outliers but retaining stragglers was followed. Table A.2 shows the data with the rejected points underlined. The means and standard deviations are calculated without these points. Inspection of the standard deviations for each component between different concentration levels does not suggest any residual anomalies.

A.4.1.2 Dependence of precision on concentration

From Table A.2, it appears that precision is related to concentration for nitrogen, but it is more difficult to judge for other components. Regression analysis is used to show whether a relationship exists, and if so, which order of polynomial is most suitable. Taking the nitrogen data, the best fit can be tested in two ways.

a) Using orthogonal coefficients (see B.10.1) and regressing standard deviation (Y-data) on concentration (X-data) and fitting to fifth order gives the following results:

Polynomial order	Orthogonal coefficient	Standard deviation	Value of t	Significance
0	4 287,556	95,943 82	44,688 19	*
1	370,199	19,393 78	19,088 54	*
2	18,342 88	4,912 924	3,733 597	ns
3	−12,868 61	1,438 596	8,945 255	ns
4	−3,713 839	0,420 389 2	8,834 288	ns
5	−0,092 463	0,170 848 9	0,541 200 5	ns

With only one degree of freedom, the t-values are compared with critical values of 12,71 at 95 %, 63,7 at 99 % and 637 at 99,9 %. Coefficients of order 2 and higher are shown to be not significant (ns), and the two adjacent ns values for orders 2 and 3 are a strong indication that the first-order equation is correct.

Fitting to first-order gives the following results:

Polynomial order	Orthogonal coefficient	Standard deviation	t-value	Significance
0	4 287,556	564,839 3	7,590 753	***
1	370,199	114,174 8	3,242 387	*

where, with five degrees of freedom, the t-values are compared with critical values of 2,571, 4,032 and 6,869. The polynomial coefficients are as follows:

$$s_i = 2\ 010{,}86 + 370{,}20x_i$$

b) Following the ANOVA approach (see B.10.2), the first-order and second-order equations are compared. The sum of squares due to regression using first-order is $2{,}347\ 9 \times 10^7$, and that using second-order is $2{,}347\ 7 \times 10^7$. The contribution made by the second-order term is 898 229, and the residual mean square from the second-order equation is 3 422 667. This gives a value for F of 0,26, which is much smaller than the tabulated value of F, which is 7,71 at the 95 % level, and hence shows that the contribution of second-order term is not significant.

Applying the F-test for significance of regression to the first-order equation produces a test statistic of 10,51. This is larger than the critical value at the 5 % level, but smaller than the 1 % value, and hence shows that the first-order regression is significant. (It is interesting to note that $\sqrt{10{,}51} = 3{,}24$, which is the t-statistic produced by orthogonal polynomials.)

Results for all test gas components are as follows:

Nitrogen	$s = 2\ 010{,}89 + 370{,}20x$
Carbon dioxide	$s = 3\ 171{,}30$
Methane	$s = 36\ 329{,}92$
Ethane	$s = 1\ 324{,}54 + 1\ 546{,}95x$
Propane	$s = 3\ 273{,}4$
Butane	$s = 1\ 410{,}3$

from which it can be seen that the standard deviation for nitrogen and ethane is related to concentration, but is sufficiently described as a constant value for the other components.

A.4.1.3 Response concentration relationship

For the analytical method to be useable, there must be a very well-defined relationship between mean response and concentration. It is important to judge whether a first-, second- or third-order equation best fits the data. Taking the nitrogen data from table A.2, the best fit can be tested in two ways.

a) Using orthogonal coefficients and regressing mean-area response (y-data) on concentration (x-data) and fitting to fifth order produced no clear decision. Fitting to fourth order gives the following results:

Polynomial order	**Orthogonal coefficient**	**Standard deviation**	**t-value**	**Significance**
0	9 359 756	6 349,898	1 474,001	***
1	1 521 421	1 283,548	1 185,324	***
2	– 2 218,781	325,154 5	6,823 774	*
3	– 267,634 4	95,211 28	2,810 952	ns
4	– 66,112 64	27,822 83	2,376 202	ns

With two degrees of freedom, the t-values are compared with critical values of 4,303 at 95 %, 9,925 at 99 % and 31,6 at 99,9 %. Coefficients of order 3 and higher are shown to be not significant (ns), and the two adjacent ns values for orders 3 and 4 are a strong indication that the second-order equation is correct.

Fitting to second-order gives the following results:

Polynomial order	**Orthogonal coefficient**	**Standard deviation**	**t-value**	**Significance**
0	9 359 756	12 519,04	747,641 7	***
1	1 521 421	2 530,559	601,219 3	***
2	– 2 218,781	641,053 2	3,461 149	*

where, with four degrees of freedom, the t-values are compared with critical values of 2,776, 4,604 and 8,610. The second-order polynomial coefficients are as follows:

$$y_i = -52\,722 + 1\,552\,995 x_i - 2\,218{,}781 x_i^2$$

b) Following the ANOVA approach, the second-order and third-order equations are compared. The sum of squares due to regression using second-order is $3{,}965\,704 \times 10^{14}$ and that using third-order is $3{,}965\,727 \times 10^{14}$. The contribution made by the third-order term is $2{,}320\,9 \times 10^{9}$, and the residual mean square from the third-order equation is $1{,}090\,9 \times 10^{9}$. This gives a value for F of 2,13, which is smaller than the tabulated value of F, which is 10,13 at the 95 % level, and hence shows that the contribution of the third-order term is not significant.

Repeating the procedure with first- and second-order equations gives a first-order sum of squares due to regression of $3{,}965\,573 \times 10^{14}$ and the previous second-order sum of squares of $3{,}965\,704 \times 10^{14}$. The contribution made by the second-order term is $1{,}305\,1 \times 10^{10}$, and the residual mean square (second-order) is $1{,}470\,7 \times 10^{9}$. The calculated F-value is 8,87, which exceeds the tabulated value of F, which is 7,71, and shows that the second-order term is significant.

The first-order coefficients were calculated so that the shapes of the polynomials could be compared. The three equations are plotted, with the individual data points, in figure A.2. It is clear from this figure that the curvature, and hence deviation from a straight line, is small.

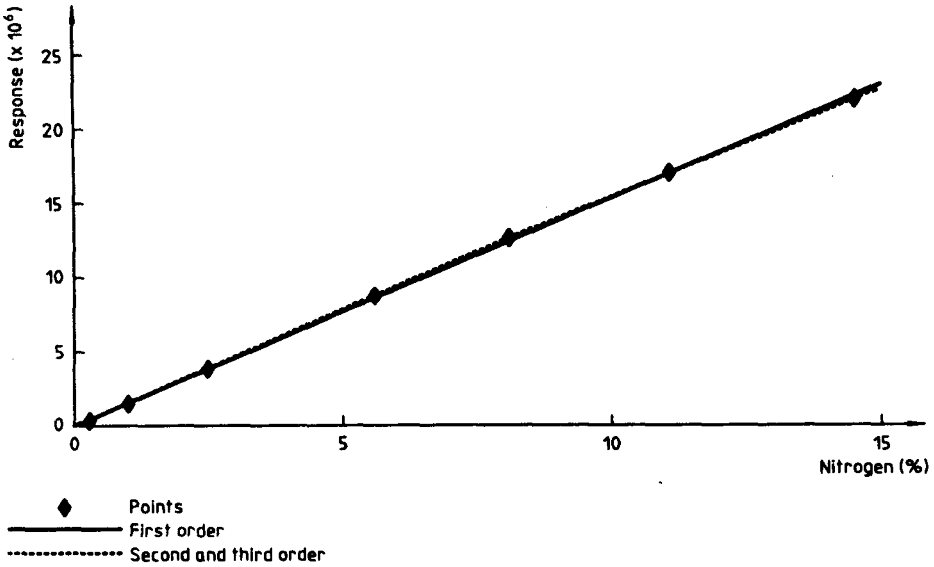

Figure A.2 — First, second and third-order fits

Results for all test gas components are as follows:

Nitrogen	$y = -52\ 722 + 1\ 552\ 995x - 2\ 218{,}78x^2$
Carbon dioxide	$y = 6\ 185{,}13 + 1\ 785\ 106x$
Methane	$y = 10\ 036\ 120 + 115\ 125x$
Ethane	$y = 71\ 026 + 2\ 107\ 404x$
Propane	$y = -18\ 683{,}3 + 2\ 645\ 461x - 20\ 767{,}8x^2$
Butane	$y = -4\ 479{,}8 + 3\ 183\ 993x - 332\ 963{,}6x^2$

Nitrogen, propane and butane require a second-order polynomial to describe their response. Over the ranges tested, carbon dioxide, methane and ethane were sufficiently described with a linear relationship. It is, however, evident from the very large non-zero intercept for methane that the first-order equation only properly represents the response over this relatively restricted range oc concentrations.

The response behaviour of *i*-butane is assumed to be similar to that of *n*-butane. Pentanes and hexanes+ are assumed, as stated earlier, to have a linear response in view of their low concentrations. The precision for these components, expressed as a standard deviation, has been assessed from repeat analyses of a natural gas. The values are as follows:

Neopentane	340
i- and *n*-Pentane	850
Hexanes+	1 700

A.4.2 Data from further calibration intervals

Where possible, the tests are repeated so as to give not less than three sets of data from different calibration intervals (e.g. operations on different days). Results should be compared between intervals and overall means derived. For the sake of space, no further information is presented here.

A.5 Component separation/interference

Inspection of the chromatogram (see figure A.1) shows that component separation, particularly for the lighter components, is very good and that there is no danger of mutual interference in this area. There is a small amount of overlap between *i*- and *n*-butane and between *i*- and *n*-pentane, but in each case the peak resolution is greater than the 1,75 minimum.

A.6 Implications of the measurements

There are two sources of error defined by these measurements. The standard deviations measured for each component indicate random day-to-day variations, and the response/concentration relationships indicate bias. These can be calculated by postulating different concentrations for standard and sample gases, and subjecting them to the measured data.

Consider two natural gases whose compositions are at the extremes of the ranges for the method. As described above, the gas used for calibration has been chosen to have a mid-range composition.

Component	**"Lean" gas**	**"Rich" gas**	**Standard**
Nitrogen	1,0	12,0	6,5
Carbon dioxide	0,1	1,0	0,6
Methane	97,6	76,77	87,16
Ethane	1,0	7,0	4,0
Propane	0,1	2,0	1,0
i-Butane	0,04	0,35	0,20
n-Butane	0,04	0,35	0,20
Neopentane	0,002	0,01	0,006
i-Pentane	0,01	0,06	0,04
n-Pentane	0,01	0,06	0,04
Hexanes+	0,1	0,40	0,25

A.6.1 Random variations

In clause A.2 it was stated that the system assumed that component response was represented by a straight line through the origin. That being so, the concentration, x_i, of a component i is calculated by the system as

$$x_i = \frac{\text{counts}_i}{\text{counts}_{\text{std}}} \times x_{\text{std}}$$

The uncertainty on x_i, expressed as a standard deviation, $s(x_i)$, is calculated as

$$\left[\frac{s(x_i)}{x_i}\right]^2 = \left[\frac{s(\text{counts}_i)}{\text{counts}_i}\right]^2 + \left[\frac{s(\text{counts}_{\text{std}})}{\text{counts}_{\text{std}}}\right]^2$$

This can be calculated for nitrogen, when analysing a sample containing 1 % using the standard containing 6,5 %, as follows:

	Concentration x	**Calculated counts**	**Calculated s(counts)**
Standard	6,5	9 948 002	4 417,2
Sample	1,0	1 498 054	2 381,1

Hence

$$\left[\frac{s(x_i)}{1}\right]^2 = \left(\frac{4\,417{,}2}{9\,948\,002}\right)^2 + \left(\frac{2\,381{,}1}{1\,498\,054}\right)^2$$

Thus

$$s(x_i) = 0{,}001\,7$$

The repeatability of measurement of x_i is calculated as

$$r(x_i) = 2{,}8\, s(x_i)$$

The repeatability is the variation on the measured value within which any two analyses of a gas would be expected to agree on 95 % of occasions. In this case,

$$r(\mathrm{N_2})(1\ \%) = 2{,}8 \times 0{,}001\,7 = 0{,}004\,6$$

Applying these calculations through out produces, for the "lean" gas

Component	**Concentration**	**Uncertainty**	
		absolute	**relative** (%)
Nitrogen	1,0	0,004 6	0,46
Carbon dioxide	0,1	0,004 9	4,9
Methane	97,6	0,121	0,12
Ethane	1,0	0,004 4	0,44
Propane	0,1	0,003 8	3,8
i-Butane	0,04	0,001 3	3,3
n-Butane	0,04	0,001 3	3,3
Neopentane	0,002	0,000 3	14,7
i-Pentane	0,01	0,000 7	7,2
n-Pentane	0,01	0,000 7	7,2
Hexanes+	0,1	0,001 5	1,5

From these compositional data, calorific value and relative density can be calculated according to the method specified in ISO 6976. This gives

Property	**Value**	**Uncertainty**	
		absolute	**relative** (%)
Calorific value	37,954	0,002 4	0,006
Relative density	0,570 9	0,000 09	0,016

Similarly, for the "rich" gas, this gives

Component	**Concentration**	**Uncertainty** absolute	**Uncertainty** relative (%)
Nitrogen	12,0	0,019	0,16
Carbon dioxide	1,0	0,010	0,96
Methane	76,77	0,106	0,14
Ethane	7,0	0,024	0,34
Propane	2,0	0,007 9	0,39
i-Butane	0,35	0,002 6	0,74
n-Butane	0,35	0,002 6	0,74
Neopentane	0,01	0,000 5	5,4
i-Pentane	0,06	0,001 3	2,1
n-Pentane	0,06	0,001 3	2,1
Hexanes+	0,40	0,002 6	0,66

Property	**Value**	**Uncertainty** absolute	**Uncertainty** relative (%)
Calorific value	37,375	0,009 8	0,026
Relative density	0,698 8	0,000 26	0,037

The only uncertainty value which exceeds the limits defined in clause A.1 is that for carbon dioxide in the "lean" gas. The value, which is underlined, is only just above the required limit. Calculated properties are well within the requirement.

When creating these "lean" and "rich" compositions, the methane figure has fallen outside the proposed analytical range, being less than 80 % in the "rich" gas and higher than 95 % in the "lean" gas. Since the uncertainty for methane is not exceeded, we may be confident that the suggested composition range will be satisfactorily measured.

A.6.2 Bias error

The magnitude of the error caused by the fact that the actual instrument response deviates from that estimated by the data handling system can be calculated from knowledge of the measured and assumed response functions, and of the concentrations in the standard and sample.

In the case of nitrogen in the "lean" gas, the "true" or measured response, $y = f(x)$, is

$$y = -52\,722 + 1\,552\,995x - 2\,218{,}78x^2$$

The data system assumes the relationship $y = g(x)$, which signifies that

$$y = k \cdot x$$

where k is a constant.

At calibration, by definition

$$\begin{aligned} y_{\text{true}} &= y_{\text{assumed}} \\ &= -52\,722 + 1\,552995x - 2\,218{,}78x^2 \\ &= k \cdot x \end{aligned}$$

Thus, the use of a 6,5 % N_2 calibration standard means that

$$k \times 6{,}5 = -52\,722 + (1\,552\,995 \times 6{,}5) - \left(2\,218{,}78 \times 6{,}5^2\right)$$

$$k = 1\,530\,462$$

The scale of the direct measurement error may be calculated using the equation

$$\varepsilon_{xN_2} = g^{-1}\left[\frac{g(x_{\text{std}})\cdot f(x_s)}{f(x_{\text{std}})}\right] - x_s$$

It is evident from the equation that the scale of error depends upont the difference between the concentrations x_{std} and x_s. Consequently, it is sensible to test the bias error with the extreme sample compositions, recognizing that compositions closer to that of the standard will produce smaller bias errors.

Application of the appropriate regression data to each component of the mixture gives the following result, for the "lean" gas:

	{	**Coefficients**	}	**Composition of standard gas**	**Composition of sample gas**	
	x^0	x^1	x^2	%	**actual** %	**measured** %
Nitrogen	– 52 722	1 552 995	– 2 218,8	6,500	1,000	0,979
Carbon dioxide	6 185,1	1 785 106	0	0,600	0,100	0,103
Methane	10 036 120	1 151 252	0	87,164	97,598	96,649
Ethane	71 026	2 107 404	0	4,000	1,000	1,025
Propane	– 18 683,3	2 645 461	– 20 767,8	1,000	0,100	0,094
i-Butane				0,200	0,040	0,040
n-Butane	– 4 479,8	3 183 993	– 332 963,6	0,200	0,040	0,040
Neopentane				0,006	0,002	0,002
i-Pentane				0,040	0,010	0,010
n-Pentane				0,040	0,010	0,010
Hexanes+				0,250	0,100	0,100
Totals				100,000	100,000	99,051

and for the "rich" gas:

	{	**Coefficients**	}	**Composition of standard gas**	**Composition of sample gas**	
	x^0	x^1	x^2	%	**actual** %	**measured** %
Nitrogen	– 52 722	1 552 995	– 2 218,8	6,500	12,000	11,933
Carbon dioxide	6 185,1	1 785 106	0	0,600	1,000	0,998
Methane	10 036 120	1 151 252	0	87,164	76,770	77,715
Ethane	71 026	2 107 404	0	4,000	7,000	6,975
Propane	18 683,3	2 645 461	20 767,8	1,000	2,000	1,991
i-Butane				0,200	0,350	0,345
n-Butane	– 4 479,8	3 183 993	– 332 963,6	0,200	0,350	0,345
Neopentane				0,006	0,010	0,010
i-Pentane				0,040	0,060	0,060
n-Pentane				0,040	0,060	0,060
Hexanes+				0,250	0,400	0,400
Totals				100,000	100,000	100,833

In neither case is the measured total equal to 100 %, and so the data would be expected to be normalized. The following tables show, in the fourth column of figures, the normalized data. The errors are calculated as the difference between the known value and the measured, normalized value, expressed in both absolute and relative terms.

Thus, for the "lean" gas:

	Standard gas	{	**Sample gas**	}	**Error**	
		actual	**measured**	**normalized**		
	%	%	%	%	**absolute**	**relative** (%)
Nitrogen	6,500	1,000	0,979	0,988	– 0,012	– 1,18
Carbon dioxide	0,600	0,100	0,103	0,104	0,004	3,86
Methane	87,164	97,598	96,649	95,575	– 0,023	– 0,02
Ethane	4,000	1,000	1,025	1,035	0,035	3,49
Propane	1,000	0,100	0,094	0,095	– 0,005	– 4,83
i-Butane	0,200	0,040	0,040	0,040	– 0,000	– 0,23
n-Butane	0,200	0,040	0,040	0,040	– 0,000	– 0,23
Neopentane	0,006	0,002	0,002	0,002	0,000	0,96
i-Pentane	0,040	0,010	0,010	0,010	0,000	0,96
n-Pentane	0,040	0,010	0,010	0,010	0,000	0,96
Hexanes+	0,250	0,100	0,100	0,101	0,001	0,96
Totals	100	100	99,051			

and for the "rich" gas:

	Standard gas	{	**Sample gas**	}	**Error**	
		actual	**measured**	**normalized**		
	%	%	%	%	**absolute**	**relative** (%)
Nitrogen	6,500	12,000	11,933	11,835	–0,165	–1,38
Carbon dioxide	0,600	1,000	0,998	0,989	– 0,011	– 1,05
Methane	87,164	76,770	77,715	77,073	0,303	0,39
Ethane	4,000	7,000	6,975	6,917	–0,083	–1,18
Propane	1,000	2,000	1,991	1,975	–0,025	–1,26
i-Butane	0,200	0,350	0,345	0,343	– 0,007	– 2,12
n-Butane	0,200	0,350	0,345	0,343	– 0,007	– 2,12
Neopentane	0,006	0,010	0,010	0,010	– 0,000	– 0,83
i-Pentane	0,040	0,060	0,060	0,060	– 0,000	– 0,83
n-Pentane	0,040	0,060	0,060	0,060	– 0,000	– 0,83
Hexanes+	0,250	0,400	0,400	0,397	– 0,003	– 0,83
Totals	100	100	100,833			

The values of physical properties calculated from these measured as normalized data can be compared with the values calculated from the known composition. This gives, for the "lean" gas:

Calorific value (known) = 37,954
Calorific value (measured) = 37,965
Difference = – 0,011 (absolute)
= – 0,03 % (relative)

Relative density (known) = 0,570 9
Relative density (measured) = 0,571 6
Difference = – 0,000 7 (absolute)
= – 0,12 % (relative)

and for the "rich" gas:

Calorific value (known) = 37,375
Calorific value (measured) = 37,388
Difference = – 0,013 (absolute)
= – 0,03 % (relative)

Relative density (known) = 0,698 8
Relative density (measured) = 0,667 0
Difference = 0,001 8 (absolute)
= 0,25 % (relative)

The figures underlined are those which exceed the component or property uncertainty levels quoted in the analytical requirement. As can be seen, there are more problems with the "rich" gas, with four components and the calculated relative density showing high uncertainty values. Only ethane and propane exceed the levels for the "lean" gas.

As acknowledged above, the methane values in these postulated compositions are outside the proposed range. It is also clear that the adjustment made by normalization, which is necessary mainly because of the non-linearity of methane response, causes the variations for other components to become worse. The calculations were repeated, with modified compositions so as to ensure that the methane concentrations did not exceed the requirement. Although there was an improvement, those components with high bias errors still gave excessive figures.

A.7 Conclusions

The repeatability of the method appears to be satisfactory, only failing to meet the uncertainty requirements for carbon dioxide in the case of the "lean" gas.

The bias error due to instrument response exceeds the acceptable limits for ethane and propane in the case of the "lean" gas, and for nitrogen, methane, ethane, propane and the calculated relative density in the case of the "rich" gas.

The bias error could be reduced by choosing standard gases which are closer to the anticipated sample compositions, or by reducing the sample size so as to minimize the curvature in the response function. A disadvantage of this latter course is that the consequent smaller signals may lead to a worsening of the repeatability.

After the method has been altered, or the new composition of the calibration gas or gases has been chosen, or both, the test procedure shall be reapplied in its entirety to see whether a satisfactory performance is now demonstrated.

Annex B
(informative)

Statistical tests and methods

It is assumed that most users of this International Standard will have access to a statistical software package, which is, in fact, necessary for polynomial regression analysis. The purpose of this annex is not to suggest an alternative to computer software, but to indicate to the user which principles are being used. If the software is less than clear as to how it is arriving at decisions or recommendations, this information may help.

B.1 Symbols and expressions used

x	Predictor or independent variable, in this case the concentration of a component. x_i is the concentration of component i.
y	Response or dependent variable, in this case the instrument response. y_i is the response from measurement of concentration x_i of component i.
n	Number of measurements in a set of data.
Σx	Sum of n values of x.
$\bar{x}$	Mean of n values of x calculated as $\bar{x} = \frac{\Sigma x}{n}$
s	Standard deviation of the values. It describes the dispersion of values around the mean, and is calculated as $s = \left[\frac{\sum (x - \bar{x})^2}{n - 1} \right]^{1/2}$
r	Estimate of repeatability.
a, b, c and d	Coefficients of regression in a polynomial equation: $y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$
$c_0, c_1, c_2, \ldots, c_m$	Orthogonal polynomial coefficients: $y = c_0 \cdot p_0(x) + c_1 \cdot p_1(x) + c_2 \cdot p_2(x) + \ldots + c_m \cdot p_m(x)$ where $c_0, c_1, c_2, \ldots, c_m$ are the orthogonal coefficients; $p_0, p_1, p_2, \ldots, p_m$ are functions of x, defined as $p_0(x) = 1$ $p_1(x) = (x - \alpha_1) \cdot p_0(x)$ $p_2(x) = (x - \alpha_2) \cdot p_1(x) - \beta_1 \cdot p_0(x)$ ...

$$p_m(x) = (x - \alpha_m) \cdot p_{m-1}(x) - \beta_{m-1} \cdot p_{m-2}(x)$$

q	Number of outliers.
$\hat{x}$	Concentration of a component calculated via the regression equation from an observed response y.
$\hat{y}$	Response equivalent to a defined component concentration, x, calculated from the regression equation.
Sxx	Sum of squares of the predictor variable calculated as $Sxx = \sum (x - \bar{x})^2$
Syy	Sum of squares of the response variable calculated as $Syy = \sum (y - \bar{y})^2$
Sxy	Sum of cross-products calculated as $Sxy = \sum \{(x - \bar{x}) \cdot (y - \bar{y})\}$
Critical value	Value from a given table against which a measured statistic is compared. The tables cover the t- and F-distributions and data for Grubbs' and Cochran's tests. The critical value is read from the table at the chosen level of probability, and at the degree or degrees of freedom equivalent to the parameters involved in the test. In some cases, more than one critical value may be required, and the test statistic compared with, for example, both the 95 % and the 99 % level.

B.2 Testing for outliers

In any set of data, individual results can be found which are not consistent with the other members of that set. These are regarded as outliers or stragglers, and should, under the correct circumstances, be eliminated from the data set. Inspection of the data is the first stage, and should identify problems such as transcription errors. The order in which tests were carried out should also be borne in mind, since rogue results may arise in cases where the previous test gas was not fully purged from the system before the first results from a new test gas are recorded.

Statistical tests are the second stage, and should be used with care, and with full understanding of the context within which the measurements were made. Removal of an apparent outlier from a set may result in a revised standard deviation for that set which is obviously much smaller than those of neighbouring sets, which were produced using similar gases during the same test period. In such a case, the apparent outlier is visible within the set, but the set containing it is not inconsistent with its neighbouring sets. It may be sensible to ignore the statistical result, and leave the value in.

Another difficulty is that an outlier test which works well with a set containing one rogue result may fail if two or more are present. Furthermore, the test should be applied differently in the case of two outliers, depending upon whether one is low and one high on the one hand, or both are low or both high on the other hand. Hence the importance of careful inspection of the data and of knowledge of how the data sets were derived.

B.2.1 Grubbs' test for a single outlier

The test statistic is calculated as

$$\frac{|x - \bar{x}|}{s}$$

where

x is the value with the highest deviation from the mean;

$\bar{x}$ is the set mean;

s is the set standard deviation.

Both $\bar{x}$ and s are calculated including the possible outlier.

The test statistic is compared with the values in table B.1. If the measured value exceeds the tabulated value at the 5 % significance level, the extreme value is a straggler. If the measured value exceeds the tabulated value at the 1 % significance level, the extreme value is an outlier.

Table B.1 — Grubbs' test for a single outlier

Number of observations	Significance level 5 % (0,05)	 1 % (0,01)
3	1,15	1,15
4	1,48	1,50
5	1,71	1,76
6	1,89	1,97
7	2,02	2,14
8	2,13	2,28
9	2,21	2,38
10	2,29	2,48
12	2,41	2,63
15	2,55	2,81
20	2,71	3,00

Test value $= \frac{|x - \bar{x}|}{s}$

where $\bar{x}$ and s are calculated including the suspected outlier.

B.2.2 Grubbs' test for two or more outliers, all high or all low

The test statistic is calculated as

$$\frac{|(\text{sum of } q \text{ outliers}) - q \cdot \bar{x}|}{s}$$

where

q is the number of outliers;

$\bar{x}$ is the set mean;

s is the set standard deviation.

Both $\bar{x}$ and s are calculated including the possible outliers.

The test statistic is compared with the values in table B.2 for the number of outliers being tested. If the measured value exceeds the tabulated value at the 5 % significance level, the extreme values are stragglers. If the measured value exceeds the tabulated value at the 1 % significance level, the extreme values are outliers.

Table B.2 — Grubbs' test for multiple outliers, all high or all low

Number of observations	Number of outliers					
	2		3		4	
	Significance level					
	5 % (0,05)	1 % (0,01)	5 % (0,05)	1 % (0,01)	5 % (0,05)	1 % (0,01)
5	2,10	2,16				
6	2,41	2,50				
7	2,66	2,79	2,97	3,08		
8	2,87	3,02	3,29	3,42		
9	3,04	3,22	3,58	3,73	3,82	3,98
10	3,18	3,40	3,82	4,00	4,17	4,34
12	3,44	3,70	4,24	4,44	4,72	4,92
14	3,66	3,92	4,57	4,83	5,20	5,42
16	3,83	4,10	4,85	5,14	5,60	5,85
18	3,96	4,25	5,08	5,38	5,91	6,20
20	4,11	4,41	5,30	5,60	6,22	6,54
30	4,56	4,92	6,03	6,41	7,26	7,64
40	4,84	5,92	6,49	6,98	7,93	8,38
50	5,06	5,51	6,82	7,34	8,38	8,88
100	5,62	6,06	7,77	8,27	9,71	10,30

$$\text{Test value} = \frac{|(\text{sum of } q \text{ outliers}) - q \cdot \bar{x}|}{s}$$

where $\bar{x}$ and s are calculated including the suspected outliers.

B.2.3 Grubbs' test for two outliers, one high and one low

The test statistic is calculated as

$$\frac{(n-1) \cdot s^2}{(n-3) \cdot s'^2}$$

where

n is the number of values in the data set;

s is the standard deviation including the possible outliers;

s' is the standard deviation excluding the possible outliers.

The test statistic is compared with the values in table B.3. If the measured value exceeds the tabulated value at the 5 % significance level, the extreme values are stragglers. If the measured value exceeds the tabulated value at the 1 % significance level, the extreme values are outliers.

This test should be used with caution, as the presence of a single substantial outlier, either high or low, can influence the test in such a way as to force a positive result, even if the value at the other extreme is a normal one. When this happens, it is invariably the case that the substantial outlier would also have been identified by a single outlier test, and the data, when retested after elimination of this point, would be shown to be normal. This test for two outliers should only be used if the earlier tests (single outlier, and two or more in one direction) have not identified any of the data points.

The results from any of the above tests which are stragglers are marked with a single asterisk (*), and outliers with a double asterisk (**). Each set of data, with any stragglers and outliers included and marked, is inspected to see whether they can be explained (transcription error, etc.) and, if appropriate, corrected. Any set which has a significantly larger number of stragglers or outliers than sets from other calibration intervals should be closely inspected, and if the behaviour cannot be satisfactorily explained, the set should be rejected. After this procedure, remaining outliers within any set should be rejected, and stragglers kept. The modified data sets are internally consistent.

Table B.3 — Grubbs' test for two outliers, one high, one low

Number of observations	Significance level	
	5 % (0,05)	1 % (0,01)
5	91	500
6	22,7	71
7	12,8	30,3
8	8,33	16,7
9	6,29	10,8
10	5,13	8,20
12	3,76	5,52
14	3,12	4,23
16	2,71	3,47
18	2,43	3,08
20	2,23	2,75
30	1,75	1,96
40	1,55	1,71
50	1,43	1,54
100	1,22	1,26

$$\text{Test value} = \frac{(n-1)\cdot S(\text{including extremes})^2}{(n-3)\cdot S(\text{excluding extremes})^2}$$

B.3 Cochran's test

This is a way of comparing sets of data between themselves to see whether any one set has a significantly larger scatter of results within it, as measured by the standard deviation, than the mean of all the sets. In this application, set standard deviations, $s_{ij1}, s_{ij2}, \ldots, s_{ijg}$ are used.

The test statistic is calculated as

$$\frac{\text{Largest variance}}{\text{Sum of variances}}$$

where variance = (standard deviation)^2.

Identify the largest standard deviation from the g sets. Assuming that it is the pth value, derive the test statistic as

$$\frac{s_{ijp}^2}{\Sigma s_{ij}^2}$$

The test statistic is compared with the values in table B.4 for Chochran's test at the 5 % and the 1 % level, using the vertical axis for the number of sets g and the horizontal axis for the number of repeats in each set f. (The test assumes the same number of repeats in each set. If there are differences between the number of repeats because of rejection of individual results due to Grubbs' test, an error will be introduced. If the differences are only one or two, the error will be small enough to be ignored.)

If the test statistic exceeds the critical value at the 5 % level, the set is a straggler: if the critical 1 % level is exceeded, the set is an outlier. Examine the data set to see whether any explanation can be found for this behaviour. In the absence of any explanation which would cause the data to be revised, a set which is a straggler is retained, but one which is an outlier is rejected. After rejection of an outlier, the remaining sets are tested again in the same way to assess the significance of the next largest variance.

Table B.4 — Cochran's maximum variance test

Number of sets	Number of repeats per set									
	2		3		4		5		6	
	Significance level									
	1 %	5 %	1 %	5 %	1 %	5 %	1 %	5 %	1 %	5 %
2			0,995	0,975	0,979	0,939	0,959	0,906	0,937	0,877
3	0,993	0,967	0,942	0,871	0,883	0,798	0,834	0,746	0,793	0,707
4	0,968	0,906	0,864	0,768	0,781	0,684	0,721	0,629	0,676	0,590
5	0,928	0,841	0,788	0,684	0,696	0,598	0,633	0,544	0,588	0,506
6	0,883	0,781	0,722	0,616	0,626	0,532	0,564	0,480	0,520	0,445
7	0,838	0,727	0,664	0,561	0,568	0,480	0,508	0,431	0,466	0,397
8	0,794	0,680	0,615	0,516	0,521	0,438	0,463	0,391	0,423	0,360
9	0,754	0,638	0,573	0,478	0,481	0,403	0,425	0,358	0,387	0,329

B.4 Repeatability

Repeatability is the value below which the absolute difference between two single test results obtained under repeatability conditions (identical test material, same method, same operator, same equipment, same laboratory and short intervals of time) may be expected to lie with a specified probability. In the absence of other indications the probability is 95 %.

Where a standard deviation of s has been measured from n repeat measurements, the repeatability, r, is calculated as

$$r = t\sqrt{2}\,s$$

with the value of t taken from the two-sided t table with $(n - 1)$ degrees of freedom. In fact, the uncertainty of measuring s means that the fine distinctions created by choosing different values of t are unjustified, and especially for the 5 % level, where the difference between single test results would be less than the calculated value 95 % of the time (19 times out of 20). In this case

$$r = 2{,}8s$$

At the 1 % level, where the difference would be less than the calculated value 99 % of the time

$$r = 3{,}7s$$

B.5 Regression analysis

The following describes the procedure for deriving the equation of a straight line by the least-squares procedure. Response curves due to second- or third-order polynomials require a computer program to derive the coefficients. The straight line has the equation $y = a + b{\cdot}x$.

B.5.1 Slope of the line

The slope of the line, b, is calculated as

$$b = \frac{Sxy}{Sxx}$$

B.5.2 Intercept

The intercept, a, is calculated as

$$a = \bar{y} - b{\cdot}\bar{x}$$

B.5.3 Sum of squares with respect to the mean

The sum of squares with respect to the mean (total sum of squares) is the sum of the differences between the observed responses and the mean response:

$$\Sigma(y_i - \bar{y})^2 = Syy$$

B.5.4 Degrees of freedom

The degrees of freedom associated with the sum of squares about the mean is $(n-1)$. Of the n values of $(y_i - \bar{y})$, only $(n-1)$ are independent, since all values of n sum to zero by definition.

B.5.5 Sum of squares due to regression

The sum of squares due to regression is the sum of the differences between the responses calculated from the regression equation and the mean response:

$$\Sigma(\hat{y}_i - \bar{y})^2 = b{\cdot}Sxy$$

In this case, where a straight line is fitted, the sum of squares due to regression has 1 degree of freedom. If higher-order polynomials are used, the degrees of freedom are the number of terms involving powers of x.

B.5.6 Sum of squares with respect to regression

The sum of squares with respect to regression (residual sum of squares) is the sum of the differences between the calculated and observed responses:

$$\Sigma(y_i - \hat{y}_i)^2 = Syy - b{\cdot}Sxy$$

The residual sum of squares has $(n-2)$ degrees of freedom, reflecting the fact that the residuals derive from a straight-line model, which requires estimation of two parameters, a and b. This rule can be extended to higher orders, which have (n–number of parameters in equation) degrees of freedom.

B.5.7 Residual mean square

The residual mean square (RMS) is the residual sum of squares divided by its degrees of freedom:

$$\text{RMS} = \frac{Syy - b{\cdot}Sxy}{n-2}$$

B.5.8 Residual standard deviation (RSD)

The residual standard deviation (RSD) is the square root of the residual mean square:

$$\text{RSD} = \left(\frac{Syy - b{\cdot}Sxy}{n-2}\right)^{1/2}$$

B.5.9 Error standard deviation

The error standard deviation (ESD) can be based on independent evidence, but is commonly taken to be identical to the RSD calculated in B.5.8.

B.6 F-test for significance of regression

This test evaluates whether the slope of the regression line is significantly different from zero. The null hypothesis is that the slope of the line is equal to zero ($H_0{:}b = 0$), which means that the best estimate of y_i is $\bar{y}$. The measured statistic is the mean square due to regression divided by the residual mean square. The mean square in each instance is the sum of squares divided by the degrees of freedom. Thus the mean square due to regression is the sum of squares (d.f.=1 in the case of a straight line), and the residual mean square is the square of the residual standard deviation:

$$F = \frac{b \cdot Sxy \cdot (n-2)}{Syy - b \cdot Sxy}$$

The measured value of F is compared with the critical value from the one-sided table at the 5 % significance level with 1 and $(n-2)$ degrees of freedom on the horizontal and vertical axes respectively. If the measured value exceeds the critical value, the null hypothesis can be rejected and the regression line can be said to be significant with a 95 % confidence level. If it does not, the null hypothesis cannot be rejected, and there appears to be no dependence of y_i on x_i. Comparison at other significance levels will increase or decrease the confidence in the line accordingly.

In the case of a straight line, or where the F-test is used on individual coefficients, the test is equivalent to a t-test for significance. This is because, at the same significance level

$$t[\text{two-sided, } (n-2) \text{ d.f.}] = \sqrt{F[\text{one-sided, } 1, (n-2)\text{d.f.}]}$$

Where such a test is used in a software package, either F or t may be quoted; their equivalence should be borne in mind.

B.7 Confidence limits for slope

This starts from the same null hypothesis (H_0:$b = 0$). Having calculated the regression equation, the range of possible values for b, the slope of the line is calculated as

$$b \pm \frac{t \cdot \text{ESD}}{\sqrt{Sxx}}$$

where t is taken from the two-sided table at the appropriate significance level and with the number of degrees of freedom associated with the residual sum of squares ($n-2$ in this case). If this range of possible values includes zero, then again the null hypothesis cannot be rejected, and y appears to be independent of x. The conclusions drawn from this test should agree with the F-test described above, since they use the same information.

B.8 Confidence limits for intercept

To test the null hypothesis that the calibration line goes through the origin (H_0:$a = 0$), the range of possible values for a, the intercept is calculated as

$$a \pm t \cdot \text{ESD} \cdot \left(\frac{1}{n} + \frac{\bar{x}^2}{Sxx} \right)^{1/2}$$

where the value of t is the same as that taken above. If the range of values includes zero, the null hypothesis cannot be rejected, and the line may be fitted through the origin.

Rearrangement of the above formula allows the t-statistic to be calculated as

$$t = \frac{a}{\text{ESD} \cdot \left(\frac{1}{n} + \frac{\bar{x}^2}{Sxx} \right)^{1/2}}$$

The measured statistic is compared with the critical value at the appropriate significance level (commonly 95 %) and $(n-2)$ degrees of freedom. If the measured value exceeds the critical value, the null hypothesis that the value of the intercept may be zero may be rejected, and the value of the intercept retained.

B.9 Equation of line through the origin

If the tests applied in clause B.8 suggest that the intercept term is not significant, the first-order equation can be modified so as to force the line to pass through the origin. For each value of concentration, x, and its related response, y, calculate the product xy and the sum of products, Σxy. Similarly, for each value of x, calculate x^2 and Σx^2. The slope of the line through the origin is given by:

$$\text{Slope} = \frac{\Sigma xy}{\Sigma x^2}$$

B.10 Polynomial regression

Although the coefficients of a first-order polynomial, of the form order $y = a + b{\cdot}x$, can be calculated using the equations described above, a computer program is necessary for second- and third-order polynomials, and so will almost certainly be used throughout. Several such programs exist, and operate satisfactorily on machines of all sizes. A suitable program will give the coefficients for the different orders of x, will provide data for, possibly in the form of an analysis of variance (ANOVA) table, which lists the sums of squares and mean squares from regression and residuals, and will perform F- or t-tests for significance. The program should give a clear indication as to the best order of polynomial, or, in the absence of clear confirmation, offer suggestions to the user on how to follow the indications.

B.10.1 Orthogonal polynomials

Orthogonal polynomials are used to avoid the disadvantage of ordinary polynomial coefficients a, b, c, etc., which are not independent of each other. They define the height of the curve, its slope and its curvature at a single point, which is the point of intersection with the y-axis. Addition of terms to, or removal of terms from, the polynomial alters the values of these coefficients. The equation of the curve can be rewritten as an orthogonal polynomial,

$$y = c_0{\cdot}p_0(x) + c_1{\cdot}p_1(x) + c_2{\cdot}p_2(x) + \ldots + c_m{\cdot}p_m(x)$$

where

$c_0, c_1, c_2, \ldots, c_m$ are the orthogonal coefficients;

$p_0, p_1, p_2, \ldots, p_m$ are functions of x, defined as

$$p_0(x) = 1$$

$$p_1(x) = (x - \alpha_1){\cdot}p_0(x)$$

$$p_2(x) = (x - \alpha_2){\cdot}p_1(x) - \beta{\cdot}p_0(x)$$

...

$$p_m(x) = (x - \alpha_m){\cdot}p_{m-1}(x) - \beta_{m-1}{\cdot}p_{m-2}(x)$$

Given this structure, the equation can be rewritten in the form

$$y = A + B{\cdot}(x + P) + C{\cdot}\left(x^2 + Q{\cdot}x + R\right) + D{\cdot}\left(x^3 + S{\cdot}x^2 + T{\cdot}x + U\right) + \ldots$$

The orthogonal coefficient c_0 represents the mean height or centre of gravity of the x data, c_1 the mean slope of the line, c_2 the mean curvature, etc. They are, therefore, mutually independent; addition of further terms does not change their values, as happens with conventional coefficients. Thus, the addition of a curvature term, c_2, does not influence the mean slope value, c_1. It is also the case that the orthogonal coefficient of order m is identical to the conventional coefficient of order m when an m-term polynomial is fitted. For a first-order polynomial, the slope, b, is identical to the mean slope, c_1. However, the intercept on the y-axis, a, is not the same as the mean of the x data, c_0. The constants $\alpha_1, \alpha_2, \ldots, \beta_1, \beta_2, \ldots$ are calculated from the x data.

$$\alpha_k = \frac{\sum (x_i \cdot p_{k-1})^2}{\sum p_{k-1}^2}$$

$$\beta_k = \frac{\sum p_k^2}{\sum p_{k-1}^2}$$

hence

$$\alpha_1 = \frac{\sum x_i}{n}$$

and

$$p_1 = x - \alpha_1$$

From p_0 and p_1, α_2 and β_1 can be derived, and so on.

Standard deviations of the orthogonal coefficients are calculated from the standard deviation of the residuals, s_R (see B.5.8), and the p terms.

For an m-term polynomial with n data points

$$s_R^2 = \frac{\sum (y_i - \hat{y}_i)^2}{n - m - 1}$$

$$s_k^2 = \frac{s_R^2}{\sum p_k^2}$$

The test statistic is calculated as

$$t_k = \frac{c_k}{s_k}$$

and is compared to tabulated values of t at the chosen level of significance.

A robust test for the best order is to establish the orthogonal polynomials for as many terms (up to 6) as are allowed by the available degrees of freedom, and to inspect the t-statistics for two adjacent non-significant values. The next lower value which is significant represents the best fit.

B.10.2 Sequential F-test

As described in the main text of this International Standard, the response function should ideally be a straight line through the origin, or something close to that. That being so, it is reasonable to use a backwards elimination procedure to test coefficients for significance. What we know of analyser behaviour leads us to doubt the good sense of rejecting a coefficient of order n while retaining one of order $(n + 1)$. Consequently, it is logical to test the coefficients for significance in the sequence: fourth order, third order, second order and finally first order. Having decided to retain a coefficient of order n, there is no point in testing one of lower order.

The fourth-order coefficient is tested so as to be sure that it does not represent an improvement over third order. If it does, the instrument response is too complicated to be useful. If, when regressing response against concentration, the first order fails to be significant, the method must be rejected. (When regressing standard deviation against concentration, of course, the first order equation may not be significant, showing that repeatability is uniform across the concentration range.)

The sequential F-test is used to judge which regression equation (first, second or third order) best describes the available data. The method consists of assessing the significance of the coefficient of the n^{th} term, assuming that all lower coefficients are already present in the regression equation.

Taking a third-order polynomial as the most complex acceptable case, the test is first applied to the coefficient of x^3 to see whether its influence is significant over the use of a third-order equation. The steps are as follows:

a) Calculate the coefficients for the fourth-order equation, and from these, calculate

- the total sum of square, $\Sigma(y_i - \bar{y})^2\{4\}$, which has $(n - 1)$ degrees of freedom;
- the sum of squares due to regression, $\Sigma(\hat{y}_i - \bar{y})^2\{4\}$, with 4 degrees of freedom;
- the residual sum of squares, $\Sigma(y_i - \hat{y}_i)^2\{4\}$, which has $(n - 5)$ degrees of freedom;
- the residual mean square, $\Sigma(y_i - \hat{y}_i)^2\{4\}/(n - 5)$.

b) Calculate the coefficients for the third-order equation, and from these, calculate

- the sum of squares due to regression, $\Sigma(\hat{y}_i - \bar{y})^2\{3\}$, with 3 degrees of freedom;
- the total sum of squares, $\Sigma(y_i - \bar{y})^2\{3\}$, is identical to that calculated in a).

c) Calculate the contribution made by the x^4 term, as the difference between the sum of squares due to regression from the fourth-order equation and that from the third-order,

$$\Sigma(\hat{y}_i - \bar{y})^2(4) - \Sigma(\hat{y}_i - \bar{y})^2(3)$$

This quantity has 1 degree of freedom.

d) Calculate F as the contribution made by the x^4 term divided by the residual mean square (RMS) from the fourth-order equation. If the value of F is greater than the critical value [one-sided table, 1 and $(n - 4)$ degrees of freedom, 95 % confidence limit], the contribution from the fourth-order term is significant and it should be retained. The response is too complex to be useable.

If the measured value is less than the critical value, the fourth-order term is not contributing significantly to the fit, and it should be rejected. The calculations are now repeated, with the third-order contribution being assessed by means of the third-order and second-order regression equations. The degrees of freedom are adjusted appropriately. This test will indicate whether the third-order term should be retained. If it is not, the second-order, and finally first-order equations are tested for significance of regression as described above.

An ANOVA table for the test on the third-order term is shown below:

Source of variation	**Degrees of freedom**	**Sum of squares**	**Mean square**	F
Total	$n - 1$	$\Sigma(y_i - \bar{y})^2\{3\}$	$\dfrac{\Sigma(y_i - \bar{y})^2\{3\}}{n - 1}$	
Regression {3}	3	$\Sigma(\hat{y}_i - \bar{y})^2\{3\}$	$\dfrac{\Sigma(\hat{y}_i - \bar{y})^2\{3\}}{3}$	$\dfrac{\text{MS}\{3\}}{\text{RMS}}$
Regression {2}	2	$\Sigma(\hat{y}_i - \bar{y})^2\{2\}$	$\dfrac{\Sigma(\hat{y}_i - \bar{y})^2\{2\}}{2}$	$\dfrac{\text{MS}\{2\}}{\text{RMS}}$
Regression {3}–{2}	1	SS{3} – SS{2}	SS{3} – SS{2}	$\dfrac{\text{SS}\{3\} - \text{SS}\{2\}}{\text{RMS}}$
Residual	$n - 4$	$\Sigma(y_i - \hat{y}_i)^2\{3\}$	$\dfrac{\Sigma(y_i - \hat{y}_i)^2\{3\}}{n - 4}$	

NOTE 4 Where possible, the same program should be used to calculate the regression equations and to calculate the sums of squares and resulting F- or t-tests. With a properly operating analyser, the sum of squares due to regression should be very much larger than the residual sum of squares, and consequently very similar to the total sum. If data are transferred manually between programs, or parts of a program, rounding errors can cause unexpected results. An example could be a negative value for the partial regression sum of squares for a particular coefficient, resulting in a negative value for F. In this case, the fact that the rounding error is possible indicates that the true value for F would probably be so small that the coefficient would be rejected.

Annex C

(informative)

Bibliography

[1] CAULCUTT, R., and BODDY, R., *Statistics for Analytical Chemists.* Chapman and Hall, London, United Kingdom.

[2] DRAPER, N.R., and SMITH, H., *Applied Regression Analysis,* Second edition. John Wiley & Sons, New York, USA.

[3] KRAGTEN, J., Least-squares polynomial curve-fitting for calibration purposes (STAT-CAL-CALIBRA), *Anal. Chim. Acta,* **241** (1990), pp. 1-13.

[4] ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory test* (now withdrawn).

TECHNICAL CORRIGENDUM 1

Page 6

Subclause 6.2

In the equation, replace s by y_s so that the equation reads:

$$x_s = \frac{y_s}{y_{std}} \times x_{std}$$

Correct the definition of x_{std} and y_{std} to read:

x_{std} is the concentration in the standard;

y_{std} is the response to the standard.

It should be noted that the expression "standard" as used here, and elsewhere in the document (e.g. subclause 6.3), means the calibration gas.

Page 13

Subclause 6.4

In the second line, correct the year of publication of ISO 7504 from 1994 to 1984.

Page 20

Table A.2 (*concluded*)

In the last column (mixture No. 307) of the second section (ethane), correct the fourth figure given for the area from 16 970 400 to 16 981 100. This part of the table will then read:

16 990 700
16 995 200
16 970 400
16 981 100
16 981 800
16 959 400

In the fourth column (mixture No. 304) of the third section (propane), correct the last figure (standard deviation) from 3468,6 to 3486,6.

In the first column (mixture No. 301) of the last section (*n*-butane), correct the last figure given for the area from 32 732 to 33 732.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 1986 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in the course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publications), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

This Indian Standard has been developed from Doc : No. PCD 24 (1857).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters :

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110 002
Telephones : 323 01 31, 323 33 75, 323 94 02

Telegrams : Manaksanstha
(Common to all offices)

Regional Offices : Telephone

Central : Manak Bhavan, 9 Bahadur Shah Zafar Marg
NEW DELHI 110 002
323 76 17
323 38 41

Eastern : 1/14 C.I.T. Scheme VII M, V. I. P. Road, Kankurgachi
KOLKATA 700 054
337 84 99, 337 85 61
337 86 26, 337 91 20

Northern : SCO 335-336, Sector 34-A, CHANDIGARH 160 022
60 38 43
60 20 25

Southern : C.I.T. Campus, IV Cross Road, CHENNAI 600 113
254 12 16, 254 14 42
254 25 19, 254 13 15

Western : Manakalaya, E9 MIDC, Marol, Andheri (East)
MUMBAI 400 093
832 92 95, 832 78 58
832 78 91, 832 78 92

Branches : AHMEDABAD. BANGALORE. BHOPAL. BHUBANESHWAR. COIMBATORE. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. KANPUR. LUCKNOW. NAGPUR. NALAGARH. PATNA. PUNE. RAJKOT. THIRUVANANTHAPURAM.

Printed at Prabhat Offset Press, New Delhi-2